

13901
26.11.55
Bm

DATE LABEL

10 DEC 1953

547.92 Eg 581
13901

Call No....547.92 Eg 581 Date...26.11.55
Account No....13901

J. & K. UNIVERSITY LIBRARY

This book should be returned on or before the last stamped above.
An overdue charges of 6 nP. will be levied for each day. The book is
kept beyond that day.

ISOMERIZATION OF PURE HYDROCARBONS

By

GUSTAV EGLOFF, GEORGE HULLA, AND V. I. KOMAREWSKY

Universal Oil Products Company

Research Laboratories

and

Illinois Institute of Technology

Chicago, Illinois



American Chemical Society
Monograph Series

REINHOLD PUBLISHING CORPORATION

330 WEST FORTY-SECOND STREET, NEW YORK, U. S. A.

1942

Oct

Oct

Oct

Copyright 1942 by

INCORPORATION SHING INCORPORATION SHING INCORPORATION SHING

reserved All rights reserved All rights reserved All rights

GLOBAL LIBRARY ALLAMA IQBAL LIBRARY ALLAMA IQBAL LIBRARY ALLAMA IQBAL LIBRARY

13901 13901 13901 13901

LIBRARY LIBRARY LIBRARY LIBRARY

Ad. 390 Ad. 390 Ad. 390 Ad. 390

26: 26: 26: 26:

SRINAGAR SRINAGAR SRINAGAR SRINAGAR

5-47-97 5-47-97 5-47-97 5-47-97

ed to Dedicated to Dedicated to Dedicat

ON T. COLONEL MARSTON T. COLONEL MARSTON T. COLONEL MARSTON T. COLONEL MARSTON

preciationwith deep appreciationwith deep appreciationWith deep ap

... ..
... ..
... ..
... ..
... ..
... ..
... ..

to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value. It was with a clear recognition of the usefulness of such work that the American Chemical Society undertook to sponsor the publication of the two series of monographs.

Two distinct purposes are served by these monographs: the first, whose fulfillment probably renders to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a form intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs enable such men to form closer contact with work in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well-digested survey of the progress already made, and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, extended references to the literature enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection is made of those papers which are most important.

AMERICAN CHEMICAL SOCIETY

BOARD OF EDITORS

HARRISON E. HOWE, *Editor of Monographs.*

Scientific Series:—

S. C. LIND,
W. MANSFIELD CLARK,
LINUS C. PAULING,
L. F. FIESER.

Technologic Series:—

WALTER A. SCHMIDT,
E. R. WEIDLEIN,
F. W. WILLARD,
W. G. WHITMAN,
C. H. MATHEWSON,
THOMAS H. CHILTON,
BRUCE K. BROWN,
W. T. READ,
CHARLES ALLEN THOMAS.

Preface

Because of its wide ramifications, isomerization is one of the most important reactions in all chemistry. The present study therefore has been confined to pure hydrocarbons of the aliphatic, alicyclic, and aromatic series. The isomerization of alkanes has developed great value from the scientific as well as the industrial standpoint. During 1941, crude oil production of the world will be over 2,000,000,000 barrels. Most of the alkanes present in the gasoline fraction are of straight-chain character, unsuitable as fuel for modern motor cars or airplanes, as they are too low in octane rating. These alkanes should be isomerized to branch-chain hydrocarbons of high antiknock properties.

One of the key hydrocarbons for the production of 100 or higher octane gasoline is isobutane, which alkylates readily with alkenes, forming isomers of heavier hydrocarbons. In natural and refinery gases the proportion of isobutane to normal averages about thirty per cent. The availability of alkenes from thermal and catalytic cracking for alkylation purposes is far greater than that of isobutane. The isomerization of *n*-butane into isobutane has developed commercially in order to supply the demand for this compound in the production of alkylate gasoline of high octane rating. The alkylates are used for blending with lower grade gasoline and tetraethyllead to produce 100 octane and higher aviation gasoline for the fighting and bombing planes of the United States and Great Britain. The United States production of this quality gasoline for 1941 is estimated at 765,000,000 gallons.

The isomerization of alkenes has industrial importance, such as the conversion of butene into isobutene and the polymerization of the latter to isoöctene motor fuel, viscous oils, or synthetic rubber. Isomerization of hydrocarbons also finds applications in the pharmaceutical, essential oil, perfume, and other industries outside of the petroleum field.

Important as the isomerization reaction is, no single theory or combination of theories adequately covers hydrocarbons. The isomerization of aliphatic hydrocarbons has made potentially available many derivatives, such as alcohols, halides, and esters.

The available experimental data have been calculated to a uniform basis wherever possible. These were thought to be of value for the purpose of comparing catalyst concentration, time, temperature, pressure, and yield of products for more than 1700 experiments on isomerization shown in thirty-six tables.

monograph.
Gustav Egloff
Chicago, Illinois
Vladimir Komarovsky

monograph.
Gustav Egloff
Chicago, Illinois
Vladimir Komarovsky

monograph.
Gustav Egloff
Chicago, Illinois
Vladimir Komarovsky

monograph.
Gustav Egloff
Chicago, Illinois
Vladimir Komarovsky

monograph.
Gustav Egloff
Chicago, Illinois
Vladimir Komarovsky

monograph.
Gustav Egloff
Chicago, Illinois
Vladimir Komarovsky

monograph.
Gustav Egloff
Chicago, Illinois
Vladimir Komarovsky

monograph.
Gustav Egloff
Chicago, Illinois
Vladimir Komarovsky

monograph.
Gustav Egloff
Chicago, Illinois
Vladimir Komarovsky

monograph.
Gustav Egloff
Chicago, Illinois
Vladimir Komarovsky

Contents

	PAGE
GENERAL INTRODUCTION	5
PREFACE	7
INTRODUCTION	13
CHAPTER I. ALKANES	
Methods Used in the Study of Isomerization	21
Isomerization of Alkanes	24
Mechanism	24
Isomerizations	28
Thermal	28
Aluminum Halides as Catalysts	28
Butanes	29
Pentanes	31
Hexanes	33
Heptanes	35
Octanes	37
Other Catalysts	40
<i>n</i> -Butane	40
<i>n</i> -Pentane	40
Hexanes	40
Heptanes	41
<i>n</i> -Octane	41
<i>n</i> -Decane	42
Conclusions	50
CHAPTER II. ALKENES, ALKADIENES, AND ALKAPOLYENES	
Isomerization of Alkenes	51
Mechanism	51
Isomerizations	55
Propene	55
Butenes	55
Pentenenes	60
Hexenes	63
Heptenes	66
Octenes	68
Decenes	69
Hexadecene	69
Conclusions	69
Alkadienes	70
Allenic Alkadienes	70
Conclusions	73
Non-Allenic Alkadienes	73
Conclusions	77
Alkapolyenes	77
Isomerizations	77
Conclusions	80

CHAPTER III. ALKYNES, ALKADIYNES, AND ALKAPOLYYNES		PAGE
Alkynes		81
Isomerizations		81
Alkadiynes and Alkapolyyne		86
Isomerizations		86
Conclusions		89
CHAPTER IV. CYCLANES, SPIRANES, BICYCLANES, AND POLYCYCLANES		
Cyclanes and Cyclanes with Saturated Side-Chains		91
Mechanism		91
Isomerizations		95
Cyclopropanes		95
Cyclobutanes		97
Cyclopentanes		97
Cyclohexanes		99
Cycloheptane and Larger Cyclanes		106
Conclusions		107
Cyclanes with Unsaturated Side-Chains		107
Mechanism		107
Isomerizations		108
Cyclopropanes		108
Cyclobutanes		108
Cyclopentanes		109
Cyclohexanes		109
Conclusions		112
Spiranes		112
Isomerizations		112
Bicyclanes and Bicyclanes with Saturated Side-Chains		112
Mechanism		112
Isomerizations		112
Bicycloheptanes		112
Bicycloöctanes		113
Bicyclononanes		113
Bicyclodecanes		113
Conclusions		115
Bicyclanes with Unsaturated Side-Chains		115
Isomerizations		115
Bicyclohexanes		115
Bicycloheptanes		116
Conclusions		120
Tricyclanes		121
Isomerizations		121
Conclusions		123
Pentacyclanes		123
CHAPTER V. CYCLENES, BICYCLENES, AND POLYCYCLENES		
Cyclenes and Cyclenes with Saturated Side-Chains		125
Isomerizations		125
Conclusions		127
Cyclenes with Unsaturated Side-Chains		127
Isomerizations		127
Conclusions		134

	PAGE
Cyclodienes with Saturated Side-Chains	134
Isomerizations	134
Cyclodienes with Unsaturated Side-Chains	135
Isomerizations	135
Conclusions	138
Bicyclenes and Bicyclenes with Saturated Side-Chains	139
Isomerizations	139
Conclusions	146
Bicyclenes with Unsaturated Side-Chains	146
Isomerizations	146
Conclusions	147
Bicyclodienes with Saturated Side-Chains	147
Isomerizations	147
Tricyclenes and Tricyclenes with Saturated Side-Chains	148
Isomerizations	148
Conclusions	149
Tricyclenes with Unsaturated Side-Chains	149
Isomerizations	149
Tetracyclenes	150
Isomerizations	150
Pentacyclenes	151
Isomerizations	151

CHAPTER VI. AROMATIC HYDROCARBONS

Alkyl Benzenes	152
Mechanism	152
Isomerizations	154
Conclusions	160
Alkenyl Benzenes	160
Mechanism	160
Isomerizations	161
Conclusions	172
Alkadienyl Benzenes	173
Allenic Alkadienyl Benzenes	173
Non-Allenic Alkadienyl Benzenes	175
Conclusions	177
Alkapolyenyl Benzenes	177
Isomerizations	177
Conclusions	180
Alkynyl Benzenes	180
Isomerizations	180
Conclusions	185
Condensed Aromatics	185
Indanes and Indenes	185
Fluorenes	189
Naphthalenes	190
Anthracenes	193
Phenanthrenes	196
Naphthacenes	197
Conclusions	198

	PAGE
Aromatic-Cyclane Hydrocarbons	199
Isomerizations	199
Conclusions	200
Aromatic-Cyclene Hydrocarbons	201
Isomerizations	201
Conclusions	212
Aromatic-Cyclodiene Hydrocarbons	213
Isomerizations	213
Conclusions	214
SUMMARY	215
Tables of Isomerization Data of	
Alkanes	218
Alkenes	244
Allenic Alkadienes	268
Non-Allenic Alkadienes	274
Alkapolyenes	280
Alkynes, Alkadiynes, and Alkapolyynes	284
Cyclanes and Cyclanes with Saturated Side-Chains	290
Cyclanes with Unsaturated Side-Chains	304
Spiranes	306
Bicyclanes and Bicyclanes with Saturated Side-Chains	308
Bicyclanes with Unsaturated Side-Chains	310
Tricyclanes	316
Cyclenes and Cyclenes with Saturated Side-Chains	318
Cyclenes with Unsaturated Side-Chains	322
Cyclodienes with Saturated Side-Chains	328
Cyclodienes with Unsaturated Side-Chains	328
Bicyclenes and Bicyclenes with Saturated Side-Chains	330
Bicyclenes with Unsaturated Side-Chains	352
Bicyclodienes with Saturated Side-Chains	352
Tricyclenes and Tricyclenes with Saturated Side-Chains	352
Tricyclenes with Unsaturated Side-Chains	354
Tetracyclenes	354
Pentacyclenes	354
Benzenes with Saturated Side-Chains	356
Alkenyl Benzenes	366
Alkadienyl Benzenes	378
Alkapolyenyl Benzenes	380
Alkynyl Benzenes	382
Condensed Aromatics (Indanes, Indenes, Fluorenes, Naphthalenes, Anthracenes, Phenanthrenes, Naphthacenes)	384
Aromatic-Cyclane Hydrocarbons	390
Aromatic-Cyclene Hydrocarbons	392
Aromatic-Cyclodiene Hydrocarbons	398
Possibilities of Hydrocarbon Isomerization as Illustrated by the Known Examples to Date	400
APPENDIX I	407
APPENDIX II	420
APPENDIX III	426
BIBLIOGRAPHY	461
AUTHOR INDEX	475
SUBJECT INDEX	483

Introduction

The hydrocarbons are assuming ever growing importance in many fields of human endeavor. Consequently, more and more emphasis will be placed upon their structures and processes of obtaining selected individual hydrocarbons. Many experiments have been conducted to change the configuration of available hydrocarbons into more desirable types. Isomerization—a fundamental molecular transformation—effects these changes without altering the number of atoms present in the molecule. This reaction has not only scientific but commercial importance in the petroleum, pharmaceutical, essential oil, perfume, and various other industries. Isomerization ramifies through the entire field of organic chemistry; hence this monograph is necessarily limited to hydrocarbons as starting materials and final products. The present study covers the isomerizations of hydrocarbons belonging to the alkane, alkene, alkyne, cyclane, cyclene, mononuclear aromatic, and polynuclear series. It endeavors to give both the qualitative and quantitative aspects of thermal and catalytic isomerizations.

Isomerization is a shift in the configuration of a molecule, without change in the number of atoms present. The formation of isomers from hydrocarbons by isomerization involves: transformations involving single, double, or triple bonds; migrations of aliphatic, alicyclic or aromatic groups; and migration or transfer of hydrogen in the molecule. There are three main classes of hydrocarbon isomerization: structural, geometrical, and optical.

Structural isomerization is the development of isomers by a formation, shifting, modification, or removal of structural units in the molecule, without change in weight. The units operated upon comprise any main aliphatic chain, its branches, all rings, their side-chains, or the unsaturated bonds located in any of these. Structural isomerization includes many complex transformations, or inter-group isomerizations, wherein the isomer product belongs to a different group. The alkanes apparently isomerize only by exchange of methyl groups for hydrogen atoms in the same molecule. Alkenes isomerize by the same transformation, by shift of the double bond, or by *cis-trans* conversion. Cyclizations of alkenes into cyclanes are seldom encountered. Alkadienes isomerize by shifts of their double bonds, by formation of an alkyne, or by cyclization. Alkapolynes have a great tendency to cyclize. Alkynes isomerize by triple-bond shift or by formation of alkadienes. Cyclanes may revert into

alkenes, change their ring-size, or redistribute their side-chains. Cyclenes are able to shift their double bond about the ring or into a side-chain. If unsaturated side-chains are attached to a cyclene, changes such as conversions into a cyclodiene, a cyclotriene (aromatization), or into a bicyclic isomer occur. The aromatics readily shift unsymmetrically located saturated side-chains. Unsaturated side-chains about various aromatic nuclei are transformed in the manner which is characteristic of unsaturated aliphatic hydrocarbons. Cyclization by closure of an unsaturated side-chain upon the aromatic nucleus is apparently aided by a facile labilization of hydrogen atoms attached to the aromatic rings. The structural isomers in general are different from the geometrical and optical "stereoisomers."

Geometrical isomerization ("*cis-trans* isomerization") is the formation of isomers having different geometrical arrangement of intact groups in the space about points of attachment where free rotation is hindered. Geometrical isomerization among the alkenes takes place under the influence of heat, sunlight, ultraviolet light, or hot acids, or upon "aging." * Cyclic hydrocarbons with hindered rotation of groups about ring carbon-atoms undergo geometrical isomerization upon the application of heat, aided by such catalysts as aluminum chloride, iodine, or nickel.

Optical isomerization is the formation of an isomer with opposite optical rotation. Optical isomerization proceeds during heating of the individual *d*- or *l*-forms. This type of isomerization, in its typical form "inversion," produces a mixture containing equal quantities of the antipodes and exhibiting a statistical optical inactivity. Such racemic mixtures can be resolved subsequently by special processes. An "asymmetrical synthesis," wherein a structurally inactive hydrocarbon forms but one optically active isomer, is generally not encountered in optical isomerization. However, optical isomers may readily isomerize to structurally inactive hydrocarbons. Optical isomers and most of the geometrical isomers, on account of structural similarity, are distinguishable only by their physical properties.

In the study of isomerization, the conditions under which the reaction proceeds deserve great consideration. In many operations of organic chemistry, isomerization results in the formation of isomers which may or may not be desirable, and facilities for controlling the process in this regard should be available. The factors affecting isomerization include: the physical states (gas, liquid, or solid) and concentrations of the initial and final hydrocarbons, concentrations and types of catalysts and sol-

* Throughout this monograph, the word "aging" is used to signify an isomerization that proceeds upon mere standing and which is presumably due to the ordinary thermal agitation of molecules.

vents, rate of reaction (contact time), temperature, pressure, agitation, irradiation, heat of activation, heat of isomerization, and free energy change. Additional factors to be considered in commercial practice are availability and cost of the initial hydrocarbon, cost and recovery of catalysts and inhibitors, and cost and yield of the isomer product.

Very little work has been done on the effect of physical states upon the course of isomerization. The formation and recovery of an isomer product may be facilitated by such operations as sublimation, distillation, and evaporation.

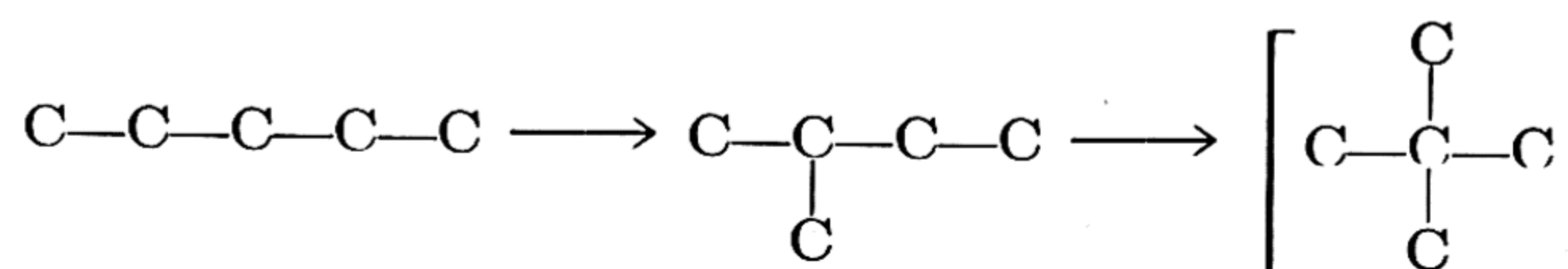
The catalyst may participate in an isomerization, either by activating the initial hydrocarbon or by forming an intermediate compound. Consequently, it seems logical to consider the types of union between the various isomers and the catalysts. Too great attraction of an isomer product for the catalyst may interfere with formation of the desired individual hydrocarbon. Preliminary investigations of effective catalysts for isomerization should include studies of their physical properties (degree of dispersion, surface activity, adsorption isotherms, lattice constants, electronic configuration) and chemical properties (valence, degree of unsaturation, degree of oxidation and reduction, acidity, alkalinity). A proper choice of catalyst may assist in the differentiation of intermediate stages of catalytic isomerization. Several examples in which acids and alkalies give cyclized and non-cyclized isomers, respectively, are considered in detail. Determinations of pH and pOH should prove valuable methods in the study of reaction reversibility involving acidity or alkalinity, respectively. Reversibility has been demonstrated also with metallic sodium and sodium ethylate (devoid of free sodium) as catalysts. When a non-specific catalyst, or two specific catalysts, accelerating reactions in opposite directions is present, the isomerization proceeds more or less reversibly, and a true equilibrium may be attained.

The isomerization rates may be regulated by adjusting the concentrations of the initial isomer, the catalyst, and the inhibitors (in the case of undesirable reactions). Short contact time should prove of value in confining the reaction to its intermediate phases. A temperature increase is synonymous with addition of energy, and an acceleration of endothermic reactions should follow its application. A proper choice of temperature may result in the formation of a desired isomer.

Application of very high pressures may aid in the formation of isomers with greater density than that of the initial hydrocarbon. For the production of symmetrical isomers, such as tetramethylmethane, pressure effects are probably of significance and should be investigated. In the few possible conversions of solid or liquid hydrocarbons into gaseous isomers, the use of a vacuum may be suggested.

Reversibility in isomerization, need for specific isomers, and possible

instability of resulting isomers introduces a selectivity factor. This factor is a function of all the reaction conditions susceptible of change. The applied sequence of reaction conditions is often of major importance. The conversion of a *n*-alkane into a highly branched isomer requires a sequence of structural changes. An appreciation of this fact may lead to the isolation of hitherto unisolated isomers, *e.g.*,



A sequence of isomerizations, such as isomer A \longrightarrow isomer B \longrightarrow isomer C, may be resolved or controlled by proper choice of catalyst and short contact time. As a general rule, the most symmetrical structural isomer or the next lower homolog (*e.g.*, 1,3,5- or 1,3-polyalkyl benzenes) and the most stable geometrical isomer (*trans*) will be formed preferentially.

Various types of side reactions are possible in the process of isomerization, due to general activation of the bonds within the molecule. The undesirable reactions include: alkylation, condensation, cracking, dealkylation, dehydrogenation, dehydrocyclization, aromatization, disproportionation, esterification, hydration, hydrogenation, oxidation, polymerization, and substitution. Side reactions in isomerization processes can be controlled by a proper choice of catalysts or by introduction of inhibitors counteracting the undesirable reactions.

Thermodynamics can be applied to isomerization of hydrocarbons since it indicates the possible (over-all) paths of isomer formation, and specifies the most favorable temperature and pressure conditions. Due to increasing movements of atoms and electrons as the temperature rises above absolute zero, no hydrocarbon can be considered perfectly stable. Furthermore, different bond strengths prevail in the molecule at the locations of C—H, C—C, C=C, or C≡C bonds. Resonance among several valence-bond structures modifies the bond energies of each type of linkage. The several bond effects are summed up or vested in a single quantity, H_T° , known as the heat of formation or "heat content" of the isomer. The importance of freedom of motion (translational, rotational, and vibrational) of the atoms comprising an isomer cannot be overlooked. This is appropriately expressed as TS_T° , which is the corresponding heat of atomic motions or the product of the entropy S_T° and the absolute temperature T . The two quantities, H_T° and TS_T° , are "opposing" potentials whose net or useful effect is known as the free energy, F_T° , of a substance. The course of any isomerization depends upon the difference, ΔF_T° , between the free energy of the final isomer and that of the initial

isomer. The free energy of isomerization, ΔF_T° , may be obtained by using any of the following formulas (involving the values of the two free energies or four corresponding "opposing" potentials):

$$\begin{aligned}\Delta F_T^\circ &= \left(H_T^\circ - TS_T^\circ \right)_{\text{final isomer}} - \left(H_T^\circ - TS_T^\circ \right)_{\text{initial isomer}} \\ &= \Delta H_T^\circ - T \Delta S_T^\circ \\ &= \left(F_T^\circ \right)_{\text{final isomer}} - \left(F_T^\circ \right)_{\text{initial isomer}}\end{aligned}$$

The equilibrium constant, which corresponds to a final steady state of isomerization, may be calculated from the thermodynamic quantities, using the following formulas:

$$\Delta H_T^\circ - T \Delta S_T^\circ = \Delta F_T^\circ$$

$$\Delta F_T^\circ = -RT \log_e K_{\text{equil.}}$$

$$\log_e K_{\text{equil.}} = -\frac{\Delta F_T^\circ}{RT} = -\frac{\Delta H_T^\circ}{RT} + \frac{\Delta S_T^\circ}{R}$$

$$\text{Antilog}_e \left(-\frac{\Delta H_T^\circ}{RT} + \frac{\Delta S_T^\circ}{R} \right) = K_{\text{equil.}}$$

$$K_{\text{equil.}} = \frac{\text{Fugacity of final isomer}}{\text{Fugacity of remaining initial isomer}}$$

where ΔH_T° = difference in heat content of isomers (the so-called "heat of isomerization" or the negative of the ordinary heat of reaction at constant pressure), in kilocalories (15°) per gram-mole. The calculation of ΔH_T° requires values of the heat of formation from carbon and hydrogen, or else the heat of combustion, for both initial isomer and final isomer. ΔH_T° is too small in value to be measured directly by ordinary calorimetry.

ΔS_T° = difference in entropy of isomers, in kilocalories (15°) per gram-mole per centigrade degree. Values of the entropy for both initial and final isomers are required. These can be measured directly by calorimetry or calculated by the methods of statistical mechanics.

ΔF_T° = difference in free energy of isomers, in kilocalories (15°) per gram-mole. ΔF_T° is obtained by subtracting $T\Delta S_T^\circ$ from ΔH_T° .

R = gas constant, in kilocalories (15°) per gram-mole per centigrade degree.

T = absolute temperature, in degrees Kelvin.

e = base of natural logarithms.

$K_{\text{equil.}}$ = equilibrium constant (approximately the ratio of partial pressures at moderate total pressure).

It is customary to report values of ΔH_T° , ΔF_T° , $T\Delta S_T^\circ$, ΔS_T° , and $K_{\text{equil.}}$ for various isomers at a standard reference temperature, 25°, and in terms of the 15° kilocalorie. The equilibrium constant is the ratio of the final isomer's fugacity to that of the remaining initial isomer. From its value several other ratios may be deduced approximately, involving the partial pressures, mole fractions, concentrations, weights,

or volumes, of the final isomer and remaining initial isomer. Thermodynamics, however, has no direct bearing upon the energy required for the activation of the initial isomer, the velocity of isomerization, or the selection of a suitable catalyst.

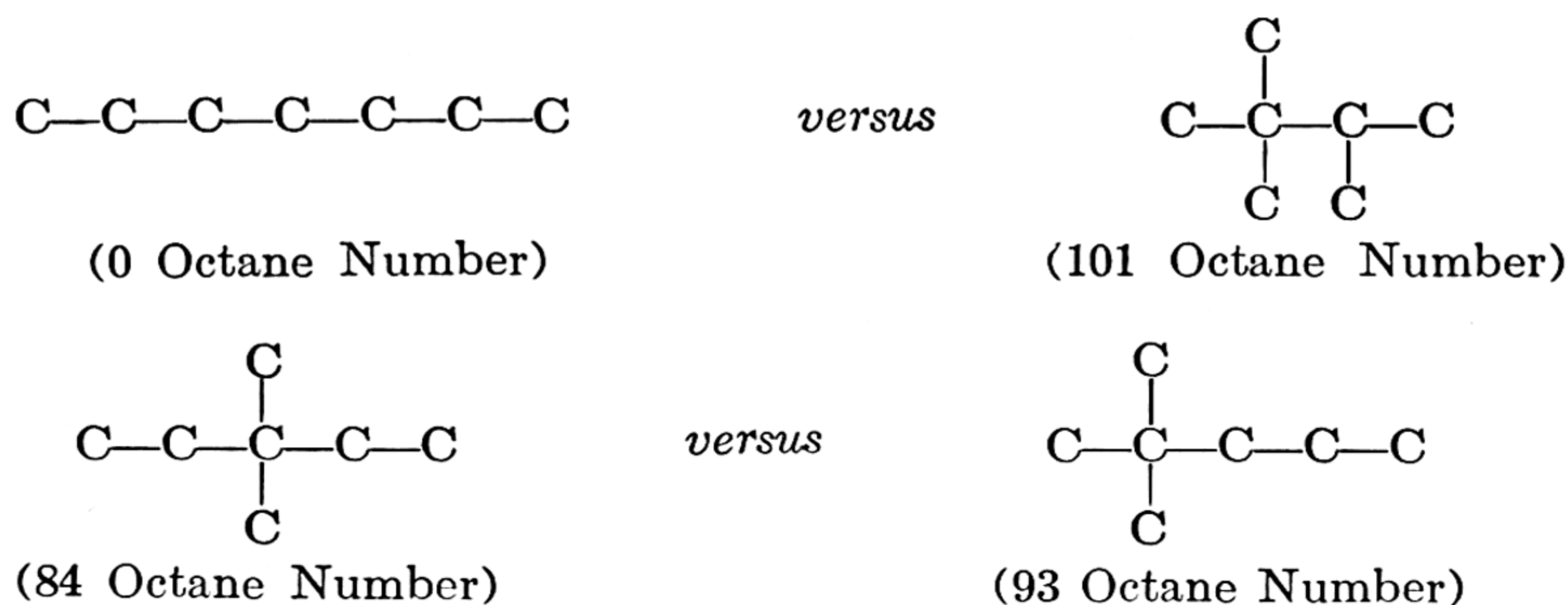
Isomerization is of theoretical and practical interest to both organic chemists and chemical physicists. Chemical and physical properties of isomers, the stability factor, and energy changes in isomerization have been of considerable concern to the chemical physicist. As a result, the concepts of chemical activity are becoming more precise. Investigations of stereochemical changes in molecules are concerned today with rotations of groups about the C—C bond, rather than with complete breaks in linkages or the related dissociation and reunion of groups. It is appropriate, therefore, to point out that the paths of isomerization are not all alike and that no single theory, or combination of theories, adequately covers the manner whereby the hydrocarbons isomerize. Although a vast amount of work has been carried out on isomers and their reactions, no well-grounded theories for alkane, cyclane, or alkyl benzene isomerizations are available. The experimental evidence in theories for alkene, alkadiene, alkyne, and cyclene isomerizations is better, because of the unsaturated or reactive character of these hydrocarbons. Since there is no general theory of isomerization, a specific theory is required for almost every type of change encountered in hydrocarbon isomerizations.

A careful examination of the many hypotheses and theories of related organic reactions has demonstrated that these are to be organized into classical and recent viewpoints. The classical points of view include the Lewis and Langmuir atom, the Baeyer strain theory, and postulated formations of addition compounds or of cyclized intermediate hydrocarbons. Only those explanations which adapt themselves readily and unequivocally are retained herein and applied to the various hydrocarbon isomerizations.

The more recent and still unconcluded mathematical viewpoints include electronic mechanics that are based principally upon wave mechanics, although quantum mechanics has its share as a related approach. On the basis of a changeable bonding for reactant and resultant, the concept of an activated complex with a mean life of 10^{-13} second is formulated. Such a molecule having a bonding approximately halfway between that of the reactant and resultant, with semi-valence or weakest bonds growing into main valence bonds and *vice versa*, cannot be readily represented. These modern viewpoints have been applied to isomerization in some cases. Their general application is prevented by the difficulty of the required methods. Electronic mechanisms may prove of importance in the future study of isomerization. The role of activated hydrocarbon molecules, intermediate activated complexes, resonance

phenomena, and kinetics of isomerization should be studied in order to obtain a better understanding and a clearer insight into the isomerization process. The lack of analytical methods, and the increasing complexity and number of possible isomers in the case of higher members of the various hydrocarbon series make the subject of isomerization more complex.

Isomerization of hydrocarbons is bound to receive a wide practical application in the petroleum industry, similar to that of polymerization, aromatization, hydrogenation, dehydrogenation, and alkylation. The tendency toward that goal follows from (1) the recognition that isomerization, by a mere change in spatial configuration of carbon and hydrogen atoms, can produce selected hydrocarbons; (2) the significance which the production of selected hydrocarbons has in aviation and, therefore, in national defense; and (3) an appreciation of the fact that the anti-knock property of motor fuels, expressed in terms of "octane number," is a function of molecular structure. It is generally recognized that chain branching in the alkanes and the orientation of their quaternary carbon atom toward the end of the molecule increase the octane number markedly, *e.g.*,



Likewise, movement of the side-chain toward the center in monomethyl alkanes increases the octane number. In the case of alkanes with one methyl group on each of two adjacent and centralized carbon atoms, the octane rating increases upon movement of the inner methyl group to the other carbon atom, *e.g.*,



When the German air force tried to invade England in September, 1940, they were stopped by the R. A. F. who were using 100 octane gasoline in their motors, whereas Germany used 87. The 100 octane gasoline gave the English superior speed and maneuverability. The isomerization reaction played a role in the quality of the gasoline used.

100 Octane vs. 87 Octane Gasoline in Airplane Performance *

Aircraft	87 Octane	100 Octane
Max. speed at 2,750 rpm	236 mph	260 mph
Altitude for max. speed	15,700 ft.	17,300 ft.
Cruising at 60% max. power at height of	192 mph 15,700 ft.	211 mph 17,300 ft.
Rate of climb at sea level	1,490 ft./min.	2,180 ft./min.
Rate of climb at 6,500 ft.	1,630 ft./min.	2,360 ft./min.
Rate of climb at 13,000 ft.	1,730 ft./min.	2,540 ft./min.
Rate of climb at 19,500 ft.	1,220 ft./min.	2,050 ft./min.
Time of climb to 6,500 ft.	4.2 min.	2.9 min.
Time of climb to 13,000 ft.	8.0 min.	5.6 min.
Time of climb to 19,500 ft.	12.3 min.	8.3 min.
Time of climb to 26,000 ft.	19.4 min.	12.2 min.
Service Ceiling	31,800 ft.	35,700 ft.
Absolute Ceiling	32,800 ft.	36,700 ft.
<i>Engine</i>		
Maximum output	830 hp	1,050 hp
Maximum power height	14,450 ft.	15,580 ft.

* The Institution of Automotive Engineers, Australia, *The Modern Engineer*, July 20, 1941.

Chapter I

Alkanes

This study discusses isomerization among all classes of hydrocarbons: alkanes, alkenes, alkynes, cyclanes, cyclenes, and aromatics.* It is appropriate that alkanes, the simplest class, be discussed first.

METHODS USED IN THE STUDY OF ISOMERIZATION

A perusal of the large number of possible structural and/or optical isomers among the alkanes (Tables 1, 2, and 3) will indicate that investigations of isomerization processes can be very complicated. A special difficulty exists in the lack of simple methods for the precise determination and identification of isomers, whose properties differ only slightly. The early methods were based upon inaccurate physical methods of separation, particularly fractional distillation of the isomerizate, followed by the comparison of a few physical constants for distillates and known isomers. At present, the separation and identification of isomers is greatly aided by recent developments in precision distillation,^{83a, 94, 94a, 442b} molecular distillation,⁶³⁶ and Raman spectra methods.^{3a, 251, 317a, 473a} The methods of the Raman spectra, Sugden's parachor,^{39a, 358a, 391a, 574c, 643a} Lorentz-Lorenz's molecular refraction,^{97a, 162a, 355c, 355d, 575a, 643a} and related (additive) "structural functions," when used along with the usual analytical procedures, may be just as essential as tables of physical properties of hydrocarbons.[†]

Great difficulty is experienced in the analysis of alkane mixtures for individual isomers. The most practical methods in use consist of precise fractional distillation, followed by identification of fractions by their melting and boiling points, densities, and refractive indices. Raman spectra methods are capable of estimating the contents of 2 or 3 alkane isomers in admixture to within 5 per cent; mixtures of 4 or more alkanes are spectroscopically unresolvable. Practically no adequate chemical

* In the literature, isomerization of hydrocarbons has been discussed principally in conjunction with their catalytic and thermal reactions,¹⁵⁵ organic catalysis,^{58a} thermal stability,¹⁵⁹ and thermodynamic properties.^{17a, 428c, 442a, 475a, 477b, 651}

† The physical constants of all known alkanes, alkenes, alkynes, and other aliphatic hydrocarbons are collated and critically evaluated in the first volume of "Physical Constants of Hydrocarbons," by Egloff¹⁵¹ (Reinhold Publishing Corp., 1939).

ISOMERIZATION OF PURE HYDROCARBONS

Table 1. Number of Isomeric Hydrocarbons of the Alkane Series
(Excluding the additional isomers due to stereoisomerism)*From Henze and Blair*²⁴⁷

Carbon Content	Number of Isomers
1	1
2	1
3	1
4	2
5	3
6	5
7	9
8	18
9	35
10	75
11	159
12	355
13	802
14	1,858
15	4,347
16	10,359
17	24,894
18	60,523
19	147,284
20	366,319
25	36,797,588
30	4,111,846,763
40	62,491,178,805,831

Note: The number of $C_{19}H_{40}$ isomers has been disputed by Perry.⁴³⁵Table 2. The Number of Structurally Isomeric Alkanes.
(Excluding the additional isomers due to stereoisomerism)*From Perry*⁴³⁵

Carbon Content	Number of Isomers
19	148,284
21	910,726
22	2,278,658
23	5,731,580
24	14,490,245
26	93,839,412
27	240,215,803
28	617,105,614
29	1,590,372,121
31	10,660,307,791
32	27,711,252,769
33	72,214,088,660
34	188,626,236,139
35	493,782,952,902
36	1,295,297,588,128
37	3,404,490,780,161
38	8,964,747,474,595
39	23,647,478,933,969
60	22,158,734,535,770,411,074,184

Table 3. Number of Stereoisomeric and Non-Stereoisomeric Alkanes.

*From Blair and Henze*⁹⁷

Carbon Content	Stereoisomers	Non-stereoisomers	Total
1	0	1	1
2	0	1	1
3	0	1	1
4	0	2	2
5	0	3	3
6	0	5	5
7	4	7	11
8	11	13	24
9	35	20	55
10	101	35	136
11	290	55	345
12	804	96	900
13	2,256	156	2,412
14	6,296	267	6,563
15	17,689	433	18,122
16	49,952	747	50,699
17	142,016	1,239	143,255
18	406,330	2,089	408,419
19	1,169,356	3,498	1,172,854
20	3,390,052	5,912	3,395,964

methods for the determination of isoalkanes are available. The Schaar-schmidt or antimony pentachloride method⁵⁰⁰ is a chemical procedure for the determination of "total isoalkanes" by means of a controlled chlorination. This method, including its modified and improved form (see Appendix I) suggested by Moldavsky and Livschitz,³⁸¹ is limited in its utility for the following reasons:

- (1) It does not identify the individual isomers.
- (2) Corrections must be made for a slower *n*-alkane chlorination that accompanies the main chlorination of isoalkanes.
- (3) Tertiary carbon atoms of hexanes are chlorinated faster than those of octanes.
- (4) Tertiary carbon atoms of octanes are chlorinated at unequal rates. 2,2,4-Trimethylpentane reacts incompletely or slowly.^{39a}
- (5) No information is given on the number of tertiary carbon atoms per molecule in a mixture of isomers.
- (6) Quaternary carbon atoms are not chlorinated, and isomers containing them without tertiary carbon atoms in the same molecule cannot be distinguished from *n*-alkanes.
- (7) Considerable disagreement^{39a, 381, 436} exists regarding the extent of substitution of chlorine for hydrogen in given alkanes.

The foregoing limitations of the antimony pentachloride method serve to stress the need of a qualitative analysis of isomer products for struc-

ture, before their quantitative estimation. Bauer ^{39a} has investigated the utility of specific and molecular parachors for the determination of alkane isomers (for method see Appendix II). The parachors were found to be "additive functions" of the number of methyl groups in the molecule. A mixture of two isomers with different numbers of methyl groups in their molecules can be analyzed quantitatively by the method of parachors. However, the method is very limited in the absence of a qualitative analysis identifying the particular isomers present. For example, it cannot distinguish between a pure methylheptane, a mixture of *n*-octane and a dimethylhexane in equal quantities, or a mixture of *n*-octane and 2,2,4-trimethylpentane in 2:1 proportions.

ISOMERIZATION OF ALKANES

Mechanism

The isomerization of alkanes, proceeding by change of carbon configuration, is accomplished by an *over-all* exchange of alkyl and hydrogen. It is an open question whether this exchange results from a direct process of rupture and recombination of the pertinent C—H and C—C bonds. The experimental evidence to date seems to favor direct rupture and recombination, due to the presence of products containing fewer and more carbon atoms than the starting material. The free radical theory of Frost, for thermal reactions in cracking, permits of an isomerization by a recombination of fragments.^{198a} However, the observed formation of over 50 per cent of isomers in several catalytic isomerizations of alkanes cannot be overlooked, since such yields appear high for a statistical redistribution of fragments, including free radicals. The following communication ^{68a} discusses the plausibility of a free radical theory for alkane isomerization:

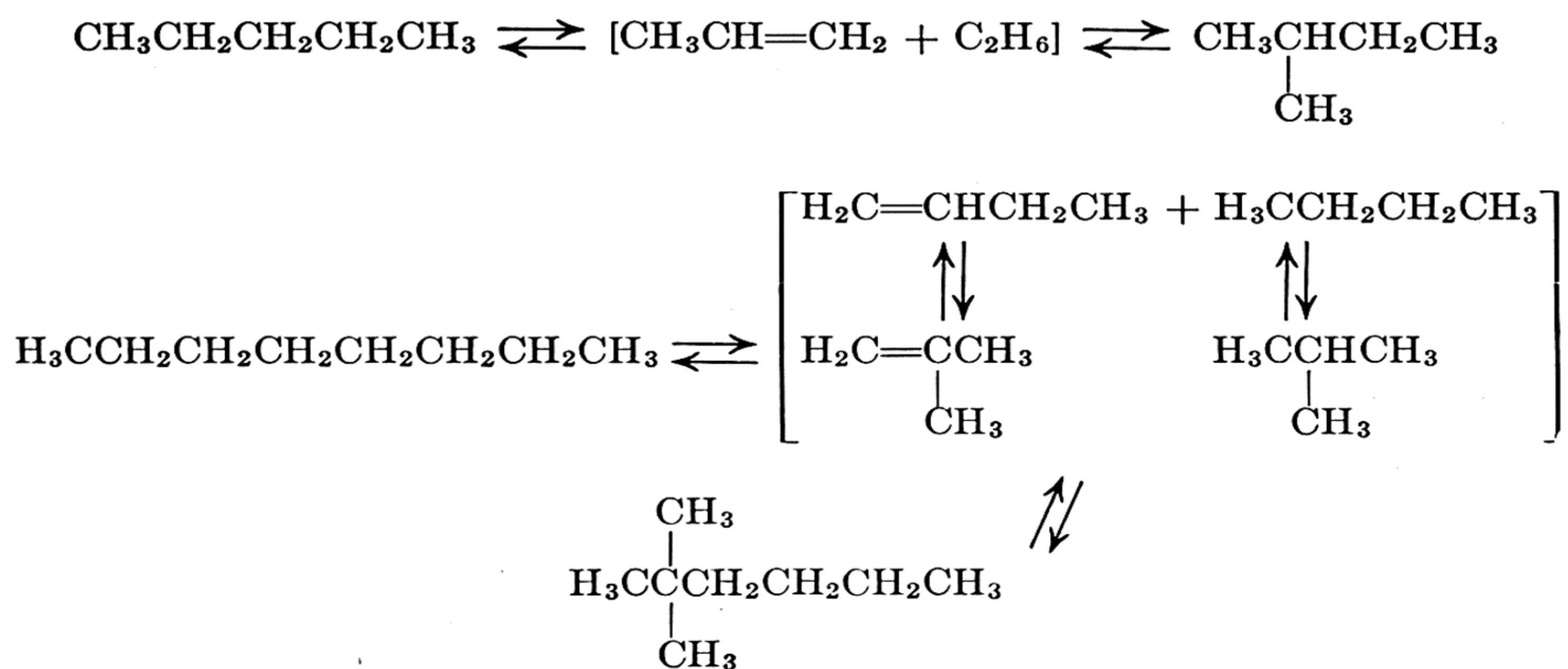
"Much more reasonable than this theory appears to be one which postulates that under the influence of a powerful catalyst the interatomic bonds of the alkane are loosened sufficiently to allow a rearrangement of the molecule as a whole to a thermodynamically more stable form by the slippage of atoms and groups of atoms *without their ever completely leaving the sphere of influence of the molecule as a whole*. Whether this bond-loosening (which may be expressed otherwise as a lowering of the activation energy of the molecule for isomerization) results from the formation of a definite hydrocarbon-catalyst complex or from the mere presence of the catalyst, through some electrical, magnetic, or dielectric influence, cannot at present be said.

"If the bonds are sufficiently loosened, as by the use of too high a temperature with a given catalyst or too powerful a catalyst at a given temperature, atoms or groups of atoms may escape completely from the

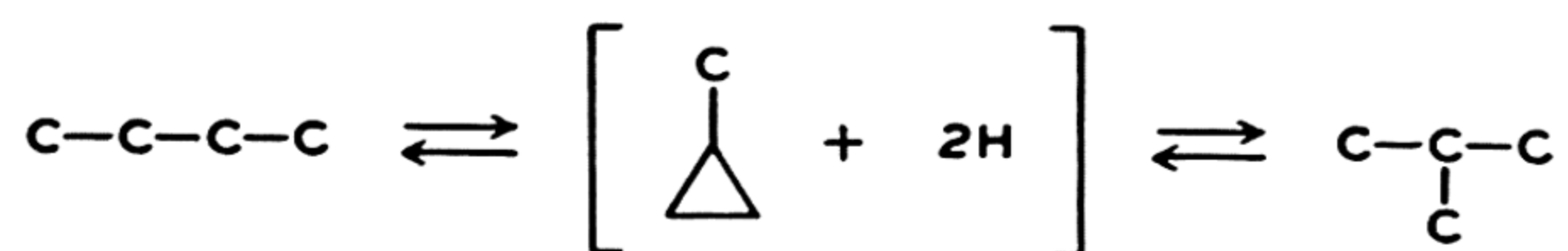
molecular field of influence and rupture (cracking) occurs, with the formation of two or more atomic aggregates relatively independent of each other. If these should recombine, an isomer of the original hydrocarbon might be formed; it is more likely, however, that if they reacted further they would do so with other molecules or fragments, producing heavier and lighter molecules than the original. Under this theory, then, isomerization and cracking result from catalytic influences which are qualitatively similar but which differ in degree."

The actual mechanism of alkane isomerization may involve one or more of the following processes:

(1) *Dealkylation* of the alkane into an alkene and an alkane, by scission of hydrogen and the rupture of a C—C bond, followed by *recombination* in a new direction (through an alkylation of the lower alkane by the alkene, or by its corresponding ester if an "acid" catalyst is present):

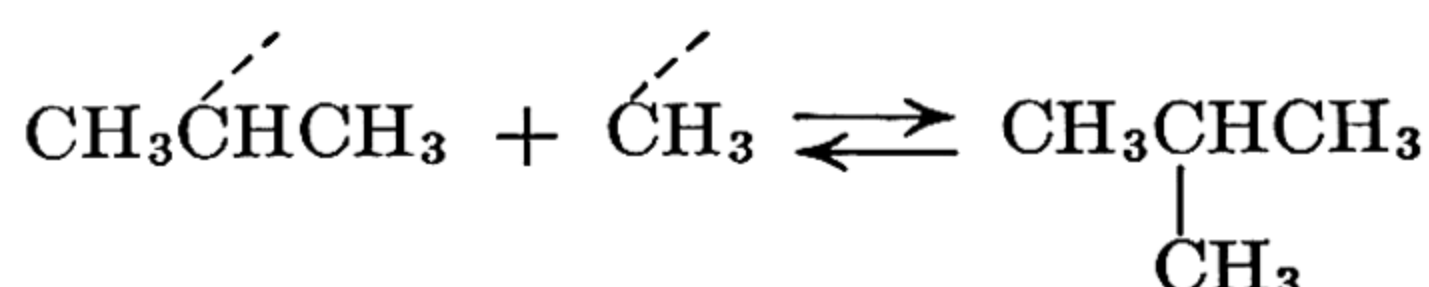
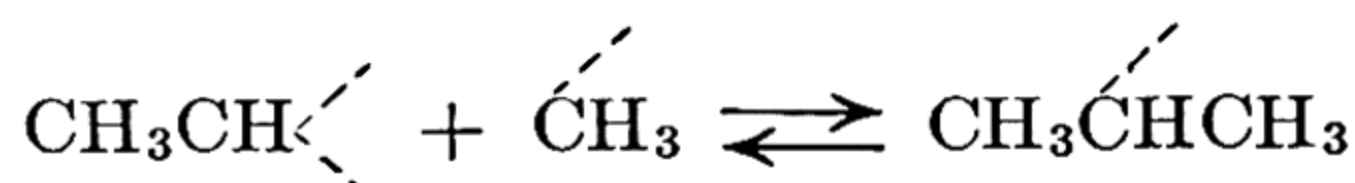
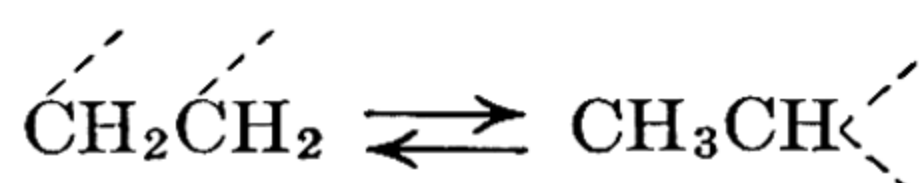
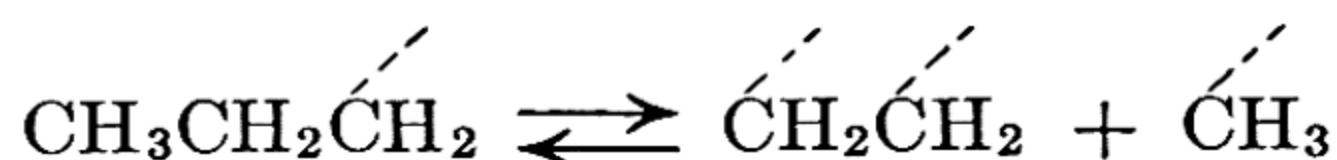
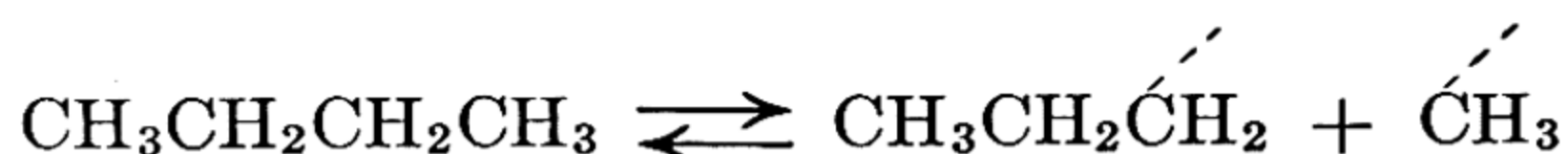


(2) *Dehydrogenation + cyclization* and subsequent *decyclization + hydrogenation* at other points in the molecule:

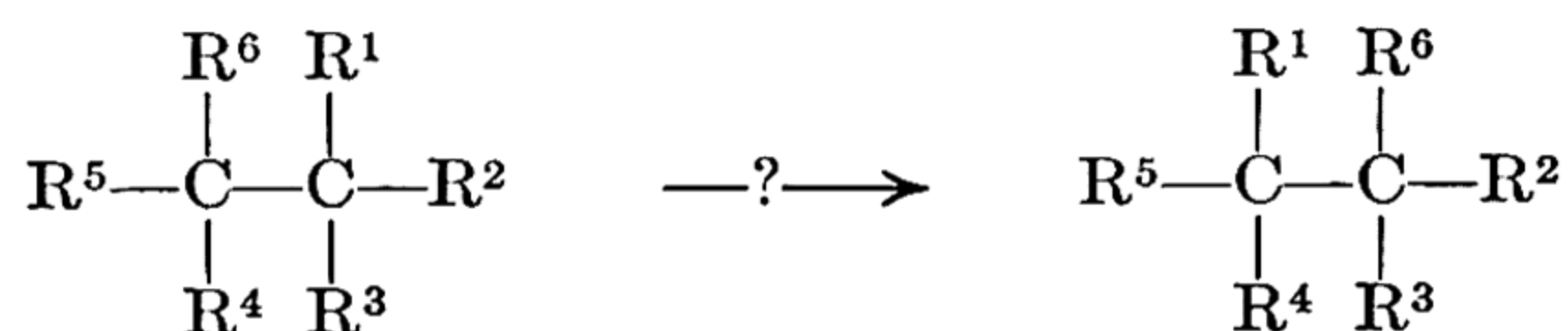


This process is considered to be a mobile system of diyl forms that seldom, if ever, attains the illustrated, cyclic "intermediate" state of transformation.

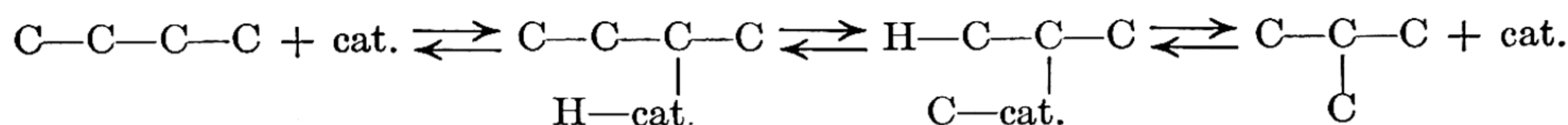
(3) *Formation of radicals* (alkyl, alkenyl, and alkylidene) and their *recombination* in new directions:



(4) *Isomerization unaccompanied by a hydrogen shifting*, as conceivable in the hexa-alkyl ethanes ($\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4, \text{R}^5, \text{R}^6$ representing combinations of alkyls):



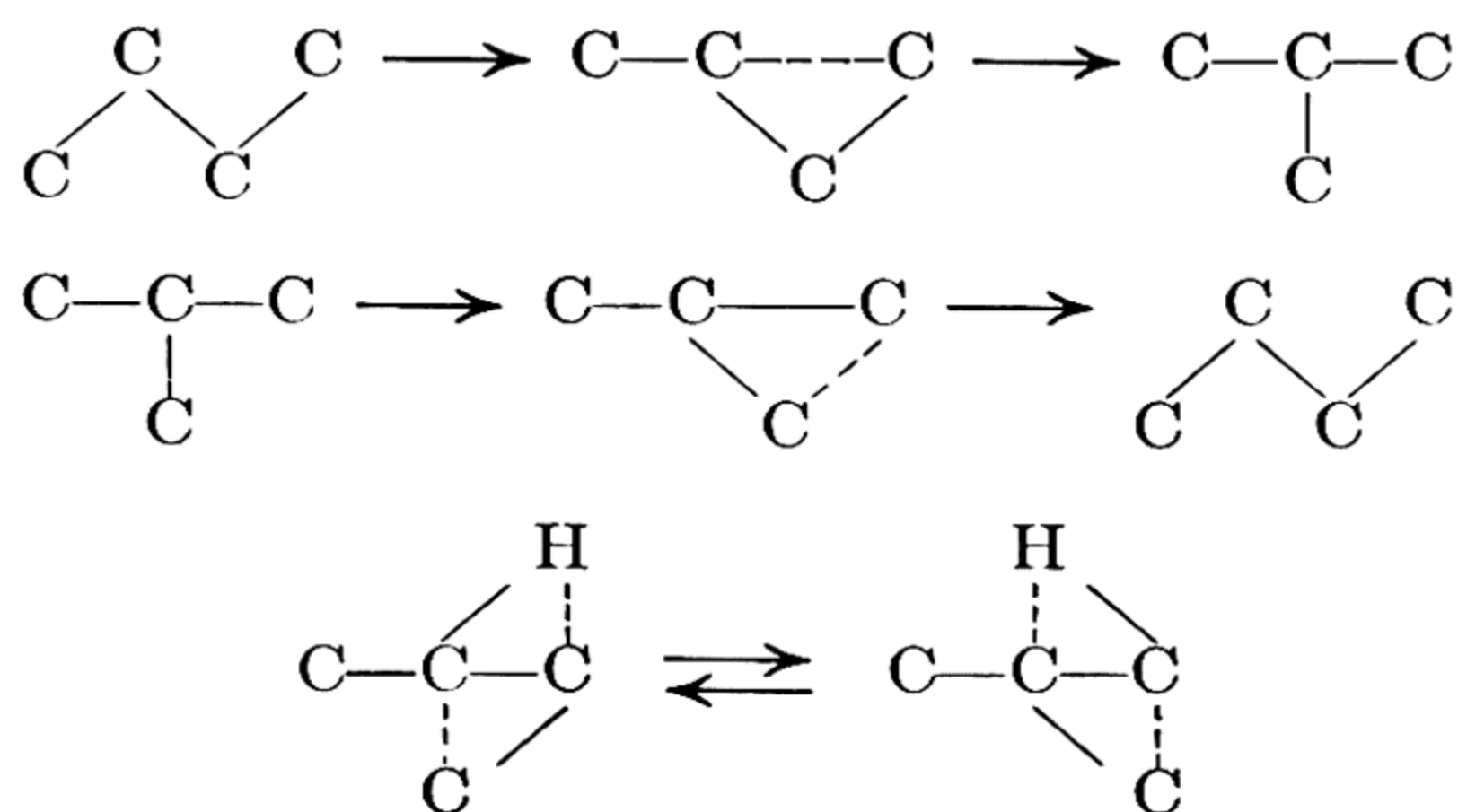
To date, none of these processes has been established in the isomerization of alkanes.* The direct alkylation of alkanes by alkenes in the presence of aluminum chloride,²⁷⁸ boron fluoride,²⁷⁷ or sulfuric acid,^{5c} together with its simplicity, favors the first explanation (Process 1). The new alkane and alkene react, probably as radicals. Alkylation of alkanes by alkenes "without any catalyst" has been observed at elevated temperature (500-510°) and pressure (306 atmospheres).^{193, 194, 424} It is of interest to consider at this point the basis of dealkylation plus alkylation leading to isomerization. With a catalyst, there may be a transfer of hydrogen and alkyl group *via* an intermediate. A general concept of the role of catalyst is an intermediate-compound formation between the hydrocarbon and the catalyst, as postulated for aluminum chloride reactions.¹⁶⁰ This should enable the reaction to proceed by a path requiring less activation energy than in the case of an uncatalyzed system, *e.g.*:



For thermal isomerization of alkanes *without a catalyst*, spatial possibilities may exist: "Compression-expansions" of the molecules and a

* There are many unsolved problems in the field of isomerization. Among these are the roles of activated hydrocarbon molecules,^{15, 402, 411, 580} intermediate activated complexes,^{131, 172, 173, 174, 210a, 200, 303a, 578a} and resonance^{429, 430, 431, 432, 433, 543, 575aa, 640a} in isomerization.

"doubling-up" in space of the molecule due to collisions of molecules, whereby transfer of hydrogen and an alkyl group is favored. These physical interpretations adapt themselves readily for the explanation of isomerization in the case of either small or large alkane molecules. A small alkane may be used as an illustration:



The mechanism of thermal isomerization, on the other hand, may be conceived as a recombination of fragments of the decomposed molecule.^{198a}

The dehydrogenation plus cyclization and subsequent decyclization plus hydrogenation (Process 2) is less favored as an explanation of alkane isomerization because it involves the migration of two hydrogen atoms. Moreover, cyclization to rings other than cyclopropanes and cyclobutanes as intermediates may give hydrocarbons of sufficient stability to resist the subsequent decyclization plus hydrogenation. Certain investigators consider substituted cyclopropanes as probable intermediates in isomerization.^{219, 220} However, there are several objections to substituted cyclopropanes as intermediates in general molecular rearrangements.* 444, 634

According to the free radical theory (Process 3), side reactions should accompany recombinations of radicals. Among free radical processes giving the same bivalent radical, it is uncertain whether dehydrogenation would precede dealkylation, or *vice versa*. Again, the postulated free radicals and reaction chains are an explanation which does not consider the role of the catalyst in isomerization. However, a catalyst may initiate the formation of a free radical, which starts the chain of reactions. The fact that the catalytic isomerization of *n*-butane yields propane, *n*-pentane, and isopentane as by-products fortifies the free radical theory

* Throughout this monograph, the word "isomerization" is used in preference to "intramolecular rearrangement" or "molecular rearrangement," because the last type of rearrangement generally requires a slight loss in final molecular composition and is usually an irreversible process, according to Porter.¹⁴³ Moreover, the term "molecular rearrangement of hydrocarbons" would be limited to movements of aliphatic, cyclic, or aromatic groups, thereby excluding many isomerizations involving a mere migration of hydrogen.

of alkane isomerization. The formation of a series of alkanes having increasing molecular weights may be the result of free radical processes occurring simultaneously or stepwise with the isomerization proper.

Changes in both C—H and C—C linkages are common to the first three processes. The recombination of fragments occurs by direct alkylation (Processes 1 and 4), hydrogenation (Process 2), or indirect alkylation (Process 3). Reversal of reaction directions in any of the first three processes should result in the formation of a *n*-alkane from its isomer, and *vice versa*. It can be stated that the isomerization of alkanes results from two over-all processes: dissociation in the presence of a catalyst, and recombination. The intermediate steps occurring in these two processes remain to be investigated completely.

Isomerizations

Thermal. There is a possibility in the numerous investigations carried out on thermal treatment of alkanes (especially at high temperatures) that isomerization takes place along with the usual cracking, dehydrogenation, and other reactions but has remained undetected because of analytical difficulties.³⁶⁸ No alkane has been observed to isomerize under strictly thermal conditions in work prior to 1937.¹⁵⁵ * However, this does not mean that non-catalytic isomerization is impossible, but rather that the subject must be studied by varying the temperature, pressure, and time of contact.

A "thermal isomerization" of *n*-octane at 450-550° in a porcelain tube has been reported recently.^{546a} The yield of isomeric octanes was poor, and further experimentation will be required to show that catalytic conditions were absent. The "subpyrogenic reactions"¹⁹⁷ of *n*-octane in a Durax glass tube at 280° to produce 2-methylheptane (?) may be considered a catalytic isomerization analogous to the established catalytic isomerization of cyclohexane in a special glass tube at 330°. ¹⁶ An optical type of alkane isomerization, such as that of *d*- or *l*-3-methylhexane, has not been studied to date. It should proceed thermally.

Aluminum Halides as Catalysts. Most of the experiments on the isomerization of alkanes have been carried out with the aid of aluminum chloride plus dry hydrogen chloride. The reaction is stated to proceed with considerable velocity at increased temperature after an induction period of about one hour (hydrogen chloride-forming) in the absence of added hydrogen chloride.³⁷⁹ However, other work ²⁷⁶ indicates the neces-

* The thermal treatment of pure alkanes has been studied for butane at 365-1100°, isobutane (400-1100°), *n*-pentane (400-1071°), isopentane (400-1075°), tetramethylmethane (575°), *n*-hexane (425-1220°), isohexane (red heat), 2,3-dimethylbutane (575°), *n*-heptane (400-1093°), *n*-octane (280-800°), 2,5-dimethylhexane (489-576°), 2,2,3,3-tetramethylbutane (450-570°), 2,7-dimethyloctane (435-550°); tridecane, tetradecane, and pentadecane (elevated temperatures), and hexadecane (390-815°).

sity of having added hydrogen chloride present. Considerable evidence¹⁶⁰ is presented to the effect that the catalysis requires both an acid, HAlCl_4 , and free aluminum chloride, although the arguments are concerned especially with the use of aluminum chloride as a catalyst for the Friedel-Crafts reaction. There is some evidence²³² that water or moisture can produce an active catalyst of the type $\text{Al}(\text{OH})\text{Cl}_2$ corresponding to the alumina hydrate, $\text{AlO}(\text{OH})$, proposed by Ipatieff as the active agent in isomerizations with alumina.²⁷⁴ * Recently,⁹⁵ the formation of isobutane as the predominant gaseous product in aluminum chloride reactions¹⁶⁰ was ascribed to the rupture of the 2,3-bond in 2,2-dimethylated structures produced by isomerization of *n*-alkanes. The formation of isobutane was presented as evidence that isomerization precedes cracking (into simpler hydrocarbons), but there is no experimental evidence in support of this simple type of mechanism.

Butanes. A direct isomerization of *n*-butane into isobutane takes place at 175° and 35 atmospheres' pressure in the presence of *anhydrous* aluminum chloride and *dry* hydrogen chloride. This reaction proceeds with a 13 per cent isobutane formation during a 4-hour reaction time.²⁷⁶ Recent patents^{604, 605} disclose the conversion of butane into isobutane (66.5 per cent) by heating for 12 hours at 150° and 30 atmospheres' pressure in the presence of aluminum chloride (16.4 per cent) and hydrogen chloride (1.6 per cent). An increase in the concentrations of aluminum chloride and hydrogen chloride caused a drop to 13.3 per cent of isobutane, due to cracking reactions.⁶⁰⁴ Another patent^{165a} discloses examples wherein mixtures of aluminum chloride with partially dehydrated preparations of alumina, silica gel, pipe clay (kaolinite), pumice, or sodium permutite (an artificial zeolite) are catalysts at $100\text{--}150^\circ$ for the isomerization of *n*-butane. The purpose of the partial dehydrations is apparently to control properly the formation of the requisite hydrogen chloride by a slow hydrolysis of aluminum chloride. A stable, granular catalyst, resistant to disintegrating influences at 200° and capable of converting *n*-butane into 53 per cent of isobutane, is prepared by mixing equal parts of anhydrous aluminum chloride and absorbent, or "activated," carbon. The catalyst is then transferred to a glass-lined pressure vessel, hydrogen chloride gas equal to 5 per cent by weight of the total mix is introduced, the pressure raised to 25 atmospheres with dry hydrogen, and the mixture heated at 250° for 3 hours with agitation.²⁸⁴ More than 50 per cent of isobutane has been obtained in the liquid-phase reaction "within a few hours" from *n*-butane with anhydrous aluminum chloride at a temperature exceeding 70° and about 4 atmospheres' partial pressure of hydrogen chloride.^{418, 420d, 422}

* Alumina is an important catalyst in organic chemistry operations. Its significance has been aptly pointed out.²⁸²

In other examples, both *n*- and isobutane were isomerized in the liquid phase at about 27° and 3 atmospheres' pressure in the presence of aluminum bromide (18.9 per cent).³⁸⁴ The isomerizations proceeded rather slowly under these conditions, and over 2 months were required to attain the equilibrium state (78-82 per cent of isobutane and 18-22 per cent of *n*-butane), starting with either of the pure hydrocarbons. Traces of methane, ethane, and propane were formed as by-products. A study of the effect of aluminum bromide concentration on the rate of isomerization of *n*-butane at 30° indicated an approximately first-order dependence on the catalyst concentration under anhydrous conditions.³⁸⁵ The rate constants were found to be between 0.030 and 0.044 mole per cent of isobutane per mole per cent of aluminum bromide per hour of treatment. Liquid-phase experiments giving a 15 per cent conversion of *n*-butane at 27° showed rate constants of 0.031-0.042 mole per cent of isobutane per mole per cent of aluminum bromide per hour in a glass vessel.³⁶⁶ Stainless-steel vessels gave higher rates of isomerization.^{366, 385} According to recent patents, *n*-butane can be isomerized in a liquid-phase reaction with 9.09 per cent by weight of aluminum bromide at 20° and 2.2 atmospheres' pressure to the extent of 1.3 per cent per hour. The converted hydrocarbon is drawn off at the top of a rectifying column attached to the reaction still, as gas containing 98-99 per cent of isobutane.^{419, 422}

A series³⁸² of experiments concerning the equilibrium between *n*-butane and isobutane at 70-180° in the presence of aluminum chloride and added hydrogen chloride has furnished an equation showing the dependence of the equilibrium constant, K_p , on absolute temperature T :

$$\log_{10} K_p = \log_{10} \frac{\text{Isobutane}}{n\text{-Butane}} = \frac{611}{T} - 1.204$$

According to this equation, the equilibrium concentrations of isobutane in the vapor state at atmospheric pressure should be 58, 63, 68, 71, and 79 per cent at 180°, 150°, 130°, 110°, and 70°, respectively. The observed equilibrium concentrations of isobutane, neglecting side reactions, amounted to 58, 63, 67, and 72 per cent at 180°, 150°, 130°, and 110°, respectively, under atmospheric pressure conditions, and to 74 per cent at 70° under the additional pressure required for a liquid phase. This equation can be compared with that corresponding to entropy values calculated for *n*-butane and isobutane by considering translational and rotational, but neglecting nuclear spin, contributions:²⁹⁸

$$\log_{10} K_p = \log_{10} \frac{\text{Isobutane}}{n\text{-Butane}} = \frac{356}{T} - 0.8991$$

Other experiments indicate that the equilibrium concentration of isobutane in the vapor state at atmospheric pressure should be 64.5, 75.8,

but only 74.8 per cent at 140°, 100°, and 60°, respectively.^{529a} The observed equilibrium concentrations of isobutane in the corresponding liquid phase, neglecting side reactions, were 64.5, 68.8, and 67.0 per cent at 140°, 100°, and 60°, respectively. One group of workers^{135a} finds that the equilibrium constant, K_p , is 2.51 at 100°, corresponding to 71.5 per cent of isobutane after correcting for side reactions. The combined results of the several data^{135a, 382, 384, 529a} on the *n*-butane-isobutane equilibrium, placed uniformly upon a vapor phase basis, can be readily shown to follow the equation:

$$\log_{10} K_p = \log_{10} \frac{\text{Isobutane}}{\text{n-Butane}} = \frac{520}{T} - 1.000$$

The exothermic heat of isomerization of *n*-butane into isobutane at 25° has been calculated as 1.63 kilocalories,⁴⁷⁵ 2.27 ± 0.20 kilocalories,¹⁹⁸ and recently as 2.20 ± 0.20 kilocalories³⁷⁵ per gram-mole. One experimenter³⁶⁶ has reported 2.10 ± 0.30 kilocalories per gram-mole for the temperature range 10-150°. This figure can be compared with 2.80 kilocalories per gram-mole for the temperature range 70-180°, which is an "average value" obtained from the experimental equilibrium equation³⁸² (*infra*) by multiplying 611 by $R \log_e 10$.

Pentanes. The isomerization of *n*-pentane into isopentane has been studied in both liquid and vapor phase with aluminum chloride plus promoters, and in the liquid phase with aluminum bromide alone.²¹⁶ No reaction was observed at atmospheric pressure when dry *n*-pentane was heated under reflux for several days with freshly sublimed aluminum chloride. Similarly, dry *n*-pentane in a vapor state, together with dry nitrogen, proved to be unreactive at 40-133° and atmospheric pressure when passed over freshly sublimed aluminum chloride. Addition of equivalent quantities of dry hydrogen bromide, dry hydrogen chloride, alkyl chlorides, hydrated aluminum chloride, or water, to aluminum chloride in the liquid-phase reaction resulted in the formation of butanes, isopentane (chief product), saturated higher-boiling products, and an insoluble unsaturated polymer. As in the work with butane,^{276, 605} it was found that the reaction with aluminum chloride takes place only in the presence of hydrogen chloride, either added directly or generated immediately afterward from aluminum chloride by the addition of water. Typical proportions for the liquid-phase reaction were given as aluminum chloride (22.9-28.3 per cent) and water (0.6-0.8 per cent), or its equivalent. Substitution of aluminum bromide for aluminum chloride gave qualitatively the same products. Aluminum bromide, being more soluble in *n*-pentane, was taken as the more active catalyst; it catalyzed "without the addition of other substances." *n*-Pentane, reacting with anhydrous aluminum bromide (9.7 per cent) at room temperature and atmospheric

pressure, gave butanes (5.0 per cent, mostly isobutane), isopentane (55.9 per cent), compounds boiling higher than *n*-pentane (3.4 per cent), and insoluble tar (0.5 per cent). Vapor-phase reaction at 40° and atmospheric pressure, using promoter substances, caused a greatly increased formation of isobutane at the expense of isopentane. Higher-boiling substances and traces of hydrogen were formed also; the most active catalyst was found to be aluminum chloride and dry hydrogen bromide. Boron fluoride is also an effective activating agent for aluminum chloride.^{37a}

Several recent patents^{603, 605} disclose the conversion of a mixture of *n*-pentane and hydrogen chloride (1.0 per cent) to isopentane (27 per cent per pass, 80 per cent upon recycling) in a continuous process utilizing aluminum chloride on active carbon at 200° and 30 atmospheres' pressure. Another patent^{420a} proposes the use of a complex compound of aluminum chloride and *tert*-butylbenzene, $C_{10}H_{14} \cdot 2AlCl_3$, as catalyst for isomerizations of *n*-pentane at 35° or 120°. Aluminum chloride catalysts, containing chlorosulfonic acid or fluorosulfonic acid, are stated to be of improved selectivity, *i.e.*, capable of preventing the formation of undesired alkenes or polymers by virtue of alkylating properties promoted by the halosulfonic acid.^{357a}

A study has been made of various mixtures of *n*-pentane and isopentane in the presence of 2 mole per cent of aluminum bromide.³⁸⁵ The results attained indicate an equilibrium concentration of isopentane near 90 per cent at 0° and between 70 and 100 per cent at 27°. Experiments on the same equilibrium, conducted in the liquid phase in the presence of aluminum chloride, hydrogen chloride, and hydrogen gas to suppress side reactions, show that the equilibrium concentration of isopentane decreases to 82 per cent at 80°. ^{529a} Other experiments ^{382a} indicate that the equilibrium concentration of isopentane in the liquid phase at 25°, 50°, 70°, and 90° is 86, 82, 78, and 74 per cent, respectively. These values have been recalculated to the vapor phase by means of Raoult's law, furnishing an equation showing the dependence of the equilibrium constant, K_p , on absolute temperature T :

$$\log_{10} K_p = \log_{10} \frac{\text{Isopentane}}{n\text{-Pentane}} = \frac{511}{T} - 0.820$$

Tetramethylmethane may be expected as a product of the isomerization of *n*-pentane or isopentane, but experimenters have not reported its presence. The unique molecular symmetry and relatively low density of tetramethylmethane warrant an investigation of the possible influence of various temperatures and absolute pressures, besides catalysts, upon isomerizations of the pentanes. An exothermic isomerization of *n*-pentane into tetramethylmethane at 25° and atmospheric pressure should occur with an energy release of 4.68 kilocalories per gram-mole.^{312, 477} This

value (4.68 kilocalories) is more than double the heat of isomerization (1.63 kilocalories) of *n*-butane into isobutane.⁴⁷⁵ This excess of energy over that for two C—C bonds may be due to stereochemical resistance in the introduction of the last methyl group. Tetramethylmethane proved to be completely stable at room temperature during 2300 hours of treatment with 5-10 mole per cent of aluminum bromide.³⁸⁵

Hexanes. *n*-Hexane, treated at its boiling point (68-69°) with aluminum chloride (27 per cent) and water (1.0 per cent) for 7.5 hours, gave a "considerable" amount of 2- and 3-methylpentanes, together with cyclohexane (1.45 per cent).⁴⁰¹ There is some doubt, however, about the resulting hydrocarbons, since the products were identified principally by their boiling points without using modern fractionation equipment. No reaction was noted when *n*-hexane was treated for 350 hours at 15-55° with aluminum chloride, unless propyl bromide was present.⁵²⁰ *n*-Hexane gave 2- and 3-methylpentanes when acted upon by aluminum bromide at room temperature.³⁶⁶

The shaking³⁷⁹ of *n*-hexane in a sealed glass tube with aluminum chloride (5 per cent) and some propyl chloride for 1-3 hours at 45-90° gave 23-28 per cent of isohexanes as determined by the antimony pentachloride method. It is claimed that propyl chloride serves only as a source of hydrogen chloride; this contradicts the viewpoint that propyl halides and aluminum chloride can be the source of a small amount of isohexanes via a Friedel-Crafts reaction.* Similar interpretations may be given for the results of experiments with propyl bromide addition.^{379, 520}

n-Hexane, subjected to the action of aluminum chloride for 3 hours at 69-73° and atmospheric pressure in the presence of hydrogen chloride, gave isohexanes (55 per cent).²⁷⁶ The isomers were isolated by fractionation and identified through their chemical properties and indices of refraction. Lower- and higher-boiling alkanes (20-25 per cent) accompanying the reaction contained isobutane (6 per cent) and pentane. The treatment of *n*-hexane in the liquid phase at 80° with aluminum chloride, hydrogen chloride, and hydrogen gas to suppress side reactions resulted in the formation of 48.4 per cent of methylpentane(s), 12.1 per cent of dimethylbutane(s), and 7 per cent of side products.^{529a} It was concluded that the true equilibrium mixture for "hexanes" in the liquid phase at 80° should contain 75 per cent of methylpentanes, 20 per cent of dimethylbutanes, and only 5 per cent of *n*-hexane. *n*-Hexane yielded almost 44 per cent of isohexanes when autoclaved at 120° for about 2 hours with aluminum chloride.^{39a} The content of isomers was

* The reactions $\text{RCl} + 2\text{R}'\text{H} \longrightarrow \text{RH} + \text{R}'\text{R}' + \text{HCl}$, and $\text{RCl} + \text{R}'\text{H} \longrightarrow \text{RH} + \text{HCl} + (\text{R}' \text{ minus H, } i.e., \text{ an alkene or cyclane})$ can be expected to result in $\text{RCl} + \text{RH} \longrightarrow \text{RR} + \text{HCl}$.

A study of the relative energy contents of the 5 hexanes indicates that isomerizations of liquid *n*-hexane at 25° and atmospheric pressure should release 1.335 ± 0.160 , 0.754 ± 0.160 , 3.446 ± 0.160 , and 1.964 ± 0.160 kilocalories per gram-mole of 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, or 2,3-dimethylbutane, respectively, formed in the reaction.^{477a} Another paper^{453a} has submitted the following corresponding values: 1.30 ± 0.21 , 0.76 ± 0.19 , 3.49 ± 0.18 , and 1.96 ± 0.20 . The heat of isomerization of *n*-hexane into 2,2-dimethylbutane is approximately that of *n*-pentane into (theoretically) tetramethylmethane. The heat of isomerization of *n*-hexane into 2,3-dimethylbutane is roughly the sum of those of *n*-hexane into 2-methylpentane and into 3-methylpentane.

Heptanes. *n*-Heptane, heated under reflux for 24 hours with aluminum chloride (26.5 per cent) and water (1.0 per cent), gave a "large amount" of isoheptanes (11 per cent?).⁴⁰¹ Other products were hydrogen chloride, propane, isobutane, pentane and hexane fractions, high-boiling cyclanes, and unsaturated hydrocarbons. *n*-Heptane, treated in various portions with ethyl, propyl, isopropyl, and *n*-butyl chlorides in the presence of aluminum chloride at room temperature, gave less than 1.7 per cent of a possible dimethylpentane and less than 2.3 per cent of a possible methylhexane.⁴⁰¹ These experiments with alkyl halides are doubtful when considered from the isomerization viewpoint; the possibility of isomers being formed from lower hydrocarbons, by an alkylation via a Friedel-Crafts reaction, has not been settled to date.

Isomerization of *n*-heptane, together with the formation of higher- and lower-boiling hydrocarbons, occurred in the presence of aluminum chloride at temperatures of 96-98°. ^{96, 97} In one of the investigations,⁹⁶ a special technique was used, consisting of a continuous withdrawal of the low-boiling products from the reaction vessel, and several additions of a small portion of aluminum chloride to the system. The product consisted of a liquid boiling in a wide range, from which 3 hexanes and 5 isomeric heptanes were isolated by fractional distillation, as shown in Table 4.*

The treatment of *n*-heptane with aluminum chloride at 40° for 5 hours in the presence of sufficient anhydrous hydrogen chloride to initially saturate the mixture, yielded 13 per cent of isomers.^{546a} Other products included 3.9 per cent of *n*-pentane plus *n*-hexane, 1.7 per cent of isopentane plus isohexanes, 2.7 per cent of higher *n*-alkanes, and 1.5 per cent of higher isoalkanes. The reaction of *n*-heptane containing 10 per

* In this survey an attempt has been made to put all experiments on a comparable basis by reporting the isomer yields in the form of per cent by weight on hydrocarbon introduced. Such measures as "cc. of product," "g. of product per cc. of charging stock," "per cent by volume," "mols per 100 mols reacted or decomposed," "mol per cent of catalyst in charging stock," and "drops or cc. of reactants" are but a step toward a quantitative formulation of "degree of isomerization."

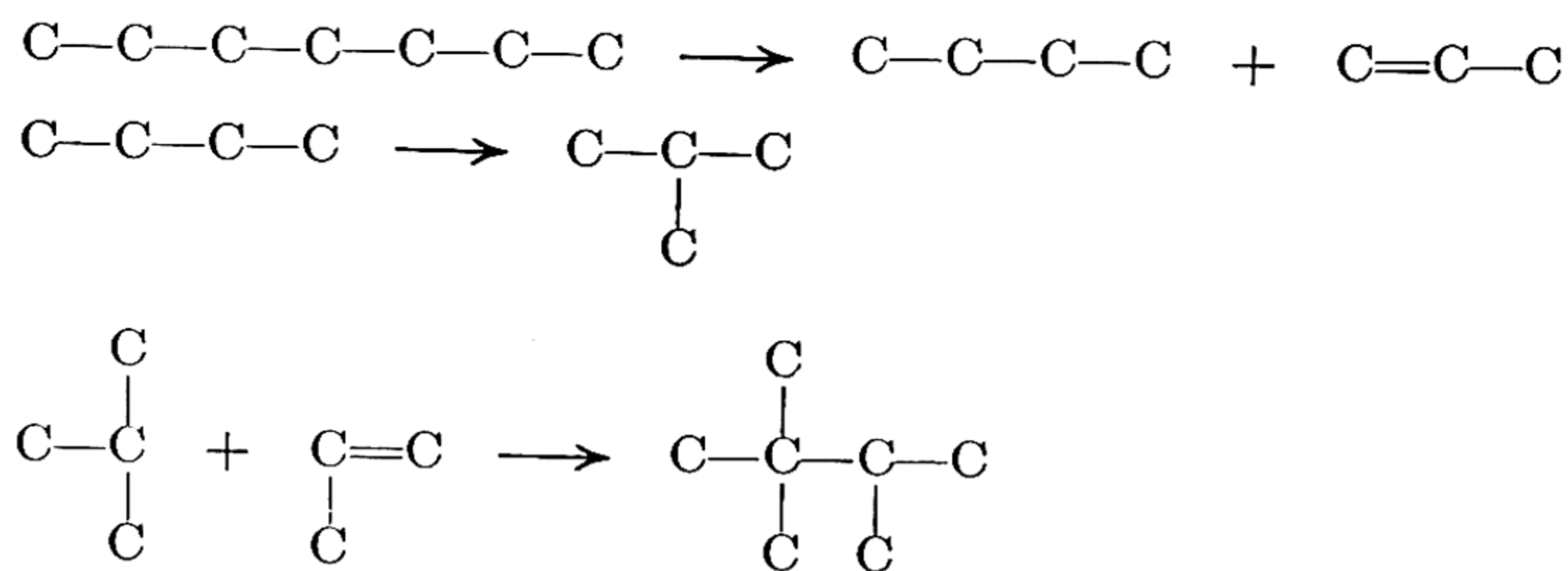
Table 4. Reaction of *n*-Heptane with Aluminum Chloride.⁹⁶

Hydrocarbons Isolated	Weight per cent on <i>n</i> -Heptane Removed	Weight per cent on <i>n</i> -Heptane Introduced
Pentanes and lower alkanes	64.6	25.84
<i>n</i> -Hexane	0.4	0.16
2-Methylpentane	3.4	1.36
3-Methylpentane	2.0	0.80
<i>n</i> -Heptane	..	60.0
2-Methylhexane	1.2	0.48
3-Methylhexane	1.6	0.64
2,4-Dimethylpentane	1.5	0.60
3,3-Dimethylpentane	0.4	0.16
2,2,3-Trimethylbutane	0.5	0.20
Polymer products	24.4	9.76
	<hr/> 100.0	<hr/> 100.0

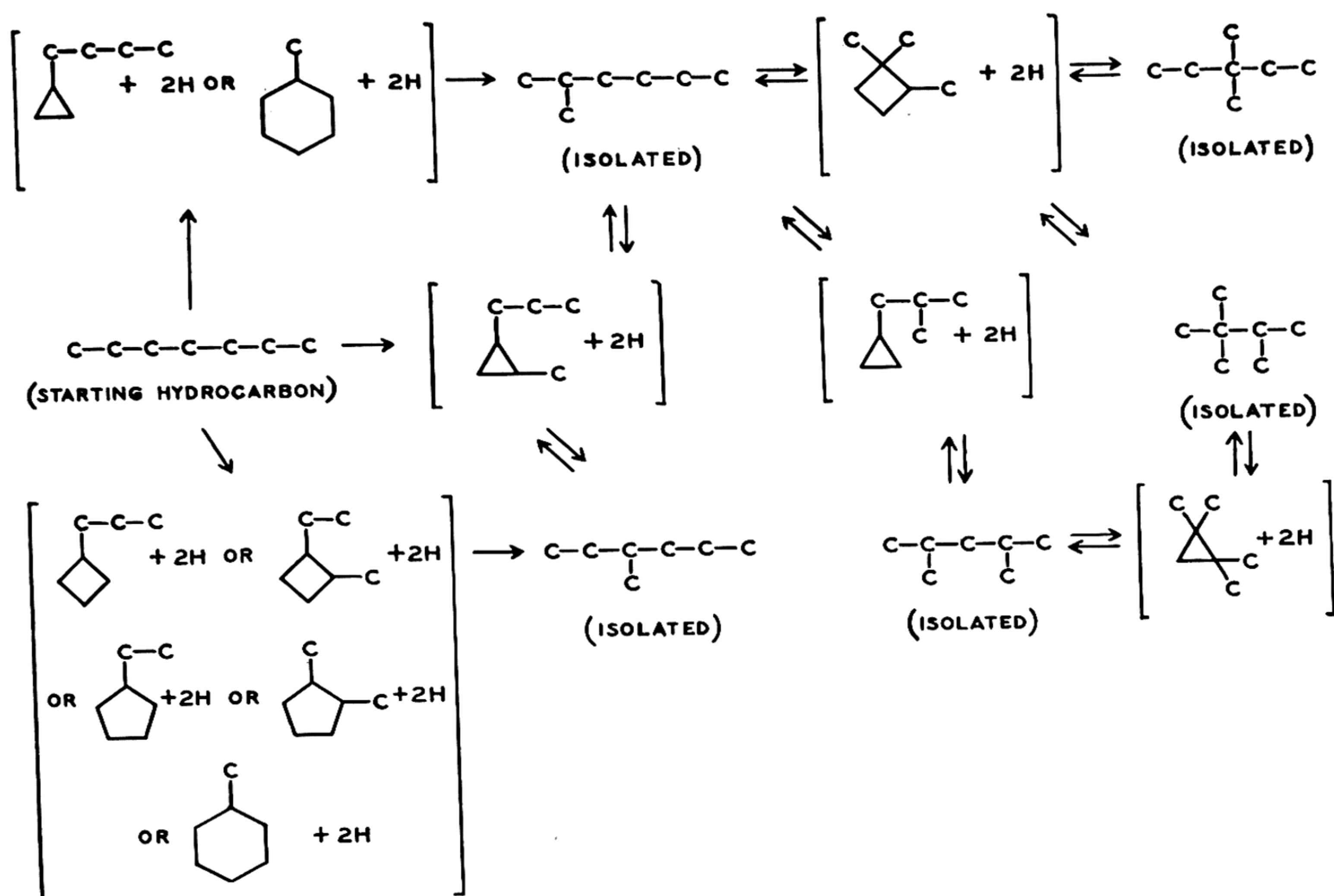
cent of its weight in aluminum chloride at 40-140°, for about 2 hours, led to the formation of 4.8-37.9 per cent of isoheptanes.^{39a} The composition of the product was determined by the method of specific parachors.

n-Heptane, heated 3 hours at 220° and 50 atmospheres' initial pressure of hydrogen in the presence of aluminum chloride (1.0 per cent), gave isoheptanes (8 per cent).⁴³⁷

Since the various isomeric heptanes in the experiments⁹⁶ conducted at the "boiling point" were isolated and identified, it is interesting to analyze the possible mechanism and complexity of the reaction. For example, the formation of 2,2,3-trimethylbutane, the extreme case of isomerization, can be explained tentatively by a mechanism given by the alkylation theory:



According to this theory, propene is an important intermediate product and some should have been isolated. The polymer products may contain incorporated propene units, which would account for its absence. However, the formation of all isomers isolated in this isomerization of *n*-heptane, similar to that of *n*-hexane, may be explained also by the theory of dehydrogenation plus cyclization and subsequent decyclization plus hydrogenation. An interpretation of the foregoing isomerizations⁹⁶ in the heptane group follows:



Nevertheless, it is difficult to account for the presence of lower hydrocarbons by a theory stressing dehydrogenation rather than dealkylation.

In view of the quest for high octane-rating branched isomers among the alkane group of gasoline hydrocarbons (*i.e.*, hexanes, heptanes, octanes, and nonanes), it is evident that the alkylation and the cyclization plus decyclization theories have much to offer in investigations of the "routes" of isomerization. The octane rating scale is based on the volume per cent of 2,2,4-trimethylpentane ("isoöctane") in *n*-heptane mixtures. Pure 2,2,4-trimethylpentane, therefore, is rated as 100 and *n*-heptane as 0 in antiknock value. In this connection, it is interesting to present in Table 5 some of the octane ratings obtained by recent investigators.^{561a} The effect of molecular structure upon the octane ratings of hydrocarbons is considered in a recent publication.^{159a}

Octanes. *n*-Octane gave no isomers when treated with freshly-sublimed aluminum chloride for 24 hours at room temperature.³⁷⁹ Saturation of the octane with hydrogen chloride effected an activation of the aluminum chloride (used 5 per cent for 22 hours and 10 per cent for 4 days) so that iso-structure octanes (24 and 61 per cent, respectively) were formed at room temperature. A 22-hour treatment of *n*-octane at room temperature with aluminum chloride (10 per cent) plus $\text{PbSO}_4 \cdot 2\text{HCl}$ or $\text{CuSO}_4 \cdot 2\text{HCl}$ (10 per cent, as sources of HCl) gave respectively 17.5 and 24.3 per cent of branched octanes. An analysis has

Table 5. Octane Numbers of Alkanes. ^{561a}

Alkanes		Octane Numbers (A. S. T. M.-C. F. R. Motor Method)
<i>n</i> -Butane	C—C—C—C	92
Isobutane	C—C—C C	99
<i>n</i> -Pentane	C—C—C—C—C	61
Isopentane	C—C—C—C C	89
Tetramethylmethane	C C—C—C C	83(?)
<i>n</i> -Hexane	C—C—C—C—C—C	25
2-Methylpentane	C—C—C—C—C C	73
3-Methylpentane	C—C—C—C—C C	75
2,2-Dimethylbutane	C C—C—C—C C	96
2,3-Dimethylbutane	C—C—C—C C C	95
<i>n</i> -Heptane	C—C—C—C—C—C—C	0
2-Methylhexane	C—C—C—C—C—C C	45
2,2-Dimethylpentane	C C—C—C—C—C C	93
2,3-Dimethylpentane	C—C—C—C—C C C	89
2,4-Dimethylpentane	C—C—C—C—C C C	82
3,3-Dimethylpentane	C C—C—C—C—C C	84

Table 5.—Continued.

Alkanes		Octane Numbers (A. S. T. M.—C. F. R. Motor Method)
2,2,3-Trimethylbutane	$ \begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C}-\text{C} \\ \quad \\ \text{C} \quad \text{C} \end{array} $	101
<i>n</i> -Octane	$ \begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array} $	—17 35
2,3-Dimethylhexane	$ \begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \quad \\ \text{C} \quad \text{C} \end{array} $	76
2,5-Dimethylhexane	$ \begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \qquad \qquad \\ \text{C} \qquad \qquad \text{C} \end{array} $	52
3,4-Dimethylhexane	$ \begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \quad \quad \\ \quad \text{C} \quad \text{C} \end{array} $	85
2,2,3-Trimethylpentane	$ \begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \quad \\ \text{C} \quad \text{C} \end{array} $	102
2,2,4-Trimethylpentane	$ \begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \qquad \quad \\ \text{C} \qquad \quad \text{C} \end{array} $	100
2,3,4-Trimethylpentane	$ \begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \quad \quad \\ \text{C} \quad \text{C} \quad \text{C} \end{array} $	97
3-Methyl-3-ethylpentane	$ \begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \quad \\ \quad \text{C}-\text{C} \end{array} $	91
2,2,3,3-Tetramethylbutane	$ \begin{array}{c} \text{C} \quad \text{C} \\ \quad \\ \text{C}-\text{C}-\text{C}-\text{C} \\ \quad \\ \text{C} \quad \text{C} \end{array} $	103

been made of the products that result when *n*-octane is acted upon by aluminum chloride at 50-55° for 6 hours in the presence of sufficient anhydrous hydrogen chloride to initially saturate the mixture.^{546a} The observed percentages of *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, and higher *n*-alkanes were 0.65, 2.6, 2.1, 43.7, and 6.66, respectively, whereas those of isopentane, isohexanes, isoheptanes, *iso*octanes, and higher isoalkanes were 0.47, 1.9, 1.6, 17.2, and 4.17, respectively. The depressed

quantities of *n*-heptane and isoheptanes are apparently indicative of a preferential scission of the octane chain between its second and third carbon atoms. *n*-Octane gave 4.7 and 12.8 per cent of isomers when subjected respectively to 20 per cent of aluminum bromide plus hydrogen bromide for 120 hours or to 20 per cent of aluminum chloride plus hydrogen chloride for 140 hours at room temperature.³⁷⁴

n-Octane, heated 3 hours at 405-410° with aluminum chloride (5 per cent) under 70 atmospheres' initial pressure of hydrogen, gave a product containing isoöctanes (23.3 per cent), together with lower- and higher-boiling hydrocarbons.⁴³⁷ In an earlier work,^{228, 571} no formation of isomers was observed from *n*-octane and from 2,5-dimethylhexane (*i.e.*, diisobutyl) under the action of aluminum chloride at 100-125°. The effect of temperature upon aluminum chloride-catalyzed isomerizations of *n*-octane can be readily seen from a series of "2-hour experiments" in which other variables were kept substantially fixed in value.^{39a} The formation of isomers increased from 4.75 to 32.6 per cent as the temperature was varied from 40° to 140°.

2-Methylheptane and 2,2,4-trimethylpentane have been isomerized at 40-140° in the presence of 10 per cent by weight of aluminum chloride.^{39a} The isomers developed during 2 hours at 140° attained a value of 16 and 15, respectively. These yields are considerably below those mentioned for *n*-octane. The content of isomers in each case was determined by the evaluation of specific parachors.

Other Catalysts. A number of catalysts have been found to isomerize alkanes, although their effectiveness varies considerably. For instance, the observation has been made⁴³⁷ that *n*-octane under controlled conditions (3 hours at 410°, 70 atmospheres' initial pressure of hydrogen) gives increasing amounts of isomers in the following order of catalysts: zinc chloride, molybdenum trisulfide, and aluminum chloride.

n-Butane. The reaction of *n*-butane in the presence of molybdenum trioxide for 8 hours at 400° and 97 atmospheres' initial pressure of hydrogen gave only 5 per cent of isobutane, along with considerably more methane, ethane, propane, and unchanged *n*-butane.²⁸³

n-Pentane. Zirconium tetrachloride in the presence of hydrogen chloride at 150° effects an isomerization of *n*-pentane into 14 per cent of isopentane.^{232a} A large quantity of isobutane, 41 per cent, is formed simultaneously.

Hexanes. The isomerization of *n*-hexane in sealed glass tubes for 6 hours at 420° was less than one per cent, without additions of catalysts, increasing to 1 and 3 per cent in the presence of molybdenum disulfide and silica, respectively.³⁸⁰ Passage of *n*-hexane at atmospheric pressure through a copper spiral at 609° gave one per cent of isomers.³⁸⁰ These isomerizations were considered as being secondary reactions, preceded

by cracking, but the arguments and evidence given are unconvincing. The isomers were identified by means of antimony pentachloride. *n*-Hexane, heated 2 hours at 400° and 90 atmospheres' initial pressure of hydrogen in a steel autoclave with 20 per cent of molybdenum disulfide, gave 27 per cent of isomers as determined by nitration.⁴⁰⁸

The agitation of 2-methylpentane for 500 hours with 96-per cent sulfuric acid gave a mixture containing 64.7 per cent of 2-methylpentane and 35.3 per cent of 3-methylpentane.³⁶⁶ An identical treatment of 3-methylpentane yielded a similar mixture with 62.5 and 37.5 per cent of 2-methylpentane and 3-methylpentane, respectively.

Heptanes. *n*-Heptane, heated 6 hours at 300° and 50 atmospheres' initial hydrogen-pressure in the presence of zinc chloride (5 per cent), gave 27 per cent of isomers as determined by antimony pentachloride, but the yield was reduced to 18 per cent of isomers in a 7 hours' treatment at 400° and 60 atmospheres' pressure of hydrogen.⁴³⁷ Fifteen per cent of isomers (by the antimony pentachloride method) were formed when *n*-heptane was heated 7 hours at 400° and 60 atmospheres' initial nitrogen-pressure in the presence of molybdenum trisulfide (5 per cent) plus cupric oxide (5 per cent).⁴³⁷ The other products of these reactions had a wide distillation range. *n*-Heptane was heated 2 hours at 400° with 9.0 per cent of molybdenum disulfide under 140 atmospheres' pressure of hydrogen, giving 11 per cent of isomers as determined by nitration and subsequent reduction.⁴⁰⁷

Heating of *n*-heptane (not pure) with molybdenum trisulfide (5 per cent) at 420° and 70 atmospheres' initial hydrogen pressure showed that isomerization increases with reaction time as follows: 11 per cent of isomers in 3 hours, 19 per cent in 7 hours, and 20 per cent in 14 hours.⁴³⁷

2,4-Dimethylpentane yielded about 15 per cent of 2,3-dimethylpentane when stirred with 97-per cent sulfuric acid for 2 hours at 50°. ^{95c} This isomerization is an interesting one, because similar primary or secondary isomerizations occur in the alkylation of isoalkanes by alkenes in the presence of sulfuric acid.^{65b, 65c} Intermediary formation of methyl hydrogen sulfate or dimethyl sulfate would partly explain these isomerizations.

n-Octane. *n*-Octane, heated 24 hours at 280° in a Durax-glass bomb tube, gave a 98-per cent yield of mixed octanes.¹⁹⁷ The isomerization was termed a "subpyrogenic reaction," but the product was not investigated thoroughly. An examination of the boiling points and densities of individual fractions comprising the mixed octanes, by reference to critically evaluated physical constants,¹⁵² indicates a mixture of *n*-octane with 2-methylheptane. There is some indication that the addition of sulfur to the *n*-octane under comparable conditions leads

momentarily to 2,3,4-trimethylpentane, since thiophthenic derivatives were isolated.¹⁹⁷ The last hydrocarbon was not isolated.

n-Octane remained unisomerized when passed through a copper spiral at 591° and atmospheric pressure or when heated 2 hours at 325° in a small silver-lined steel pressure apparatus.³⁸⁰ Pressure treatment of *n*-octane with the silver-lined steel apparatus at 450° gave 6 and 9 per cent of isomers in 2 and 3.7 hours, respectively.³⁸⁰ Removal of the silver lining resulted in 11 per cent of isomers at 450°, whereas use of a large steel autoclave at 475° gave 10 per cent.³⁸⁰ These "isomerizations" were considered to be the result of secondary reactions among products from a preliminary cracking.

n-Octane, heated 3 hours at 410° under 70 atmospheres' initial hydrogen-pressure in the presence of zinc chloride (5 per cent), gave 11.7 per cent of isomers (by the antimony pentachloride method).⁴³⁷ Heating of *n*-octane for 3 hours under 70 atmospheres' initial hydrogen pressure in the presence of molybdenum trisulfide (5 per cent) gave no change at all at 360°, but formed 18 and 23.6 per cent of isomers (determined by the antimony pentachloride method) at 410° and 440°, respectively.⁴³⁷ Unsaturated and aromatic hydrocarbons totaled 8 per cent at 440°, indicating that considerable cracking occurs at the point of maximum isomerization. All these reactions gave products with a wide distillation range.

It has been found that isomerization of *n*-octane takes place in the presence of certain dehydrogenation catalysts at 300-310° and atmospheric pressure.⁶⁵⁹ Catalysis with nickel-alumina, and platinum on activated carbon, resulted in the formation of 5.5 and 15 per cent of isomers, respectively. Nickel on zinc oxide was tested also, giving 6.4 per cent of isomers. The first two experiments are particularly interesting, since no unsaturates were found in the reaction products. Alumina or activated carbon alone produced 4 per cent of isomers from *n*-octane at 310°. ⁶⁵⁹ The isomers were determined by the antimony pentachloride method. *n*-Octane, passed over alumina at 300-310° under atmospheric pressure, gave 10-12 per cent of isomers as determined by the antimony pentachloride method.³¹⁸

n-Decane. *n*-Decane in the presence of nickel-alumina at 350° formed 1.6 per cent of isomers (determined by the antimony pentachloride method), together with 6 per cent of aromatics whose formation was due to a dehydrogenation plus cyclization.³¹⁹

It must be noticed that the isomerization of *n*-octane and *n*-decane in the presence of a *dehydrogenating* catalyst terminates without formation of unsaturates other than those of aromatics; the product has a very narrow boiling range and seems to consist of unchanged alkane, iso-alkanes, and aromatics. This fact must not be overlooked; it implies

that higher alkane isomerization may occur by dehydrogenation to an alkane, followed by isomerization to an isoalkene, and this succeeded by a disproportionation to an isomeric alkane and an aromatic. Numerous examples are known wherein unsaturated hydrocarbons undergo an irreversible disproportionation into more-saturated and less-saturated hydrocarbons in the presence of dehydrogenating catalysts.^{70, 71, 95b, 121, 125, 150, 218, 221, 303b, 336a, 340, 341, 342, 344, 346, 347, 348, 350b, 350c, 358b, 358c, 359, 361, 428b, 467, 480a, 540a, 540b, 594a, 645a, 663a, 663b, 664, 665, 669a, 671a, 671b}

The past few years have seen a large advancement in thermodynamic data applicable to isomerization of hydrocarbons. It is appropriate, therefore, to submit a summary of the work that has been done on the alkanes to date. A recent paper^{477b} has reported values of comparative thermodynamic quantities for the butanes, pentanes, hexanes, and heptanes, all in the ideal gaseous state, at temperatures ranging from 25° to 727°; these values are reproduced in Table 5a.

From these data, Figures 1-10 were plotted^{477b} as a function of the absolute temperature. Figures 1-4 show which of the isomers is thermodynamically the most stable (lowest value of $\frac{\Delta F_T^\circ}{T}$), which is the least stable (highest value of $\frac{\Delta F_T^\circ}{T}$), and give the stability order of the intermediate isomers. The ordinate designation, $\Delta F^\circ/T$ in cal/(deg mole), corresponds to this monograph's $\frac{\Delta F_T^\circ}{T}$ in gram-calories per gram-mole per degree Kelvin. Figures 5-8 show how one mole of alkane molecules distribute themselves among the various isomeric forms at thermodynamic equilibrium in the gaseous state from 260 to 1060° K., for those pressures where the ratio of fugacity to pressure is substantially the same for the given isomers. The vertical width of a band at a given temperature measures the equilibrium mole fraction of the indicated isomer present in the gas phase. Figures 9-10 compare the available data on the direct determinations of the equilibrium concentrations of *n*-butane and isobutane, as well as *n*-pentane and isopentane, with the values for the same quantities (solid line) derived from the summarized data (*infra*).

From the foregoing data, the following statements were drawn with regard to the isomerization of butanes, pentanes, hexanes, and heptanes in the gaseous state:^{477b}

“(a) At 25° C., the normal isomer is thermodynamically the least stable in each case, with the exception that 3-ethylpentane is less stable than *n*-heptane.

“(b) Relative to the other isomers, the normal isomer increases in

(Text cont'd on p. 50)

Table 5a. Summary of Values of the Thermodynamic Function $\Delta F_T^\circ/T$ in gram-calories per gram-mole per degree Kelvin, the Corresponding Equilibrium Constants $K = \text{Fugacity of Isomer/Fugacity of } n\text{-Alkane}$, and the Corresponding Equilibrium Concentrations N in Mole Fraction of the Total Isomerizate, for the Isomerization of the Butanes, Pentanes, Hexanes, and Heptanes in the Ideal Gaseous State, from 298° to 1000°K. (Rossini, Prosen, and Pitzer)

Temperature		Butanes						Pentanes								
		<i>n</i> -Butane			Isobutane			<i>n</i> -Pentane			2-Methylbutane			2,2-Dimethylpropane		
<i>t</i> °C.	<i>T</i> °K.	$\frac{\Delta F_T^\circ}{T}$	<i>K</i>	<i>N</i>	$\frac{\Delta F_T^\circ}{T}$	<i>K</i>	<i>N</i>	$\frac{\Delta F_T^\circ}{T}$	<i>K</i>	<i>N</i>	$\frac{\Delta F_T^\circ}{T}$	<i>K</i>	<i>N</i>	$\frac{\Delta F_T^\circ}{T}$	<i>K</i>	<i>N</i>
25	298	0	1	0.28	-1.86	2.55	0.72	0	1	0.03	-5.28	14.3	0.44	-5.65	17.1	0.53
127	400	0	1	0.44	-0.47	1.27	0.56	0	1	0.11	-3.64	6.23	0.65	-1.65	2.30	0.24
227	500	0	1	0.54	0.35	0.84	0.46	0	1	0.18	-2.68	3.86	0.69	0.59	0.74	0.13
327	600	0	1	0.60	0.83	0.66	0.40	0	1	0.24	-2.11	2.89	0.67	1.98	0.37	0.087
527	800	0	1	0.68	1.44	0.48	0.32	0	1	0.32	-1.38	2.00	0.63	3.75	0.15	0.048
727	1000	0	1	0.72	1.86	0.39	0.28	0	1	0.37	-0.92	1.59	0.59	4.78	0.09	0.034

Temperature		Hexanes						2,3-Dimethylbutane								
		<i>n</i> -Hexane			2-Methylpentane			3-Methylpentane			2,2-Dimethylbutane			2,3-Dimethylbutane		
<i>t</i> °C.	<i>T</i> °K.	$\frac{\Delta F_T^\circ}{T}$	<i>K</i>	<i>N</i>	$\frac{\Delta F_T^\circ}{T}$	<i>K</i>	<i>N</i>	$\frac{\Delta F_T^\circ}{T}$	<i>K</i>	<i>N</i>	$\frac{\Delta F_T^\circ}{T}$	<i>K</i>	<i>N</i>	$\frac{\Delta F_T^\circ}{T}$	<i>K</i>	<i>N</i>
25	298	0	1	0.013	-3.33	5.34	0.071	-1.25	1.88	0.025	-8.22	62.6	0.84	-2.78	4.05	0.054
127	400	0	1	0.061	-1.98	2.71	0.16	-0.43	1.24	0.075	-4.58	10.0	0.61	-0.81	1.51	0.092
227	500	0	1	0.13	-1.25	1.88	0.24	0.09	0.96	0.12	-2.37	3.30	0.41	0.35	0.84	0.105
327	600	0	1	0.19	-0.74	1.45	0.27	0.39	0.82	0.15	-0.91	1.58	0.29	1.14	0.56	0.104
527	800	0	1	0.26	-0.15	1.08	0.28	0.72	0.70	0.18	0.75	0.69	0.18	1.99	0.37	0.096
727	1000	0	1	0.31	0.24	0.89	0.27	0.86	0.65	0.20	1.68	0.43	0.13	2.49	0.29	0.088

Temperature		Heptanes												2,2,3-Trimethylbutane														
		<i>n</i> -Heptane			2-Methylhexane			3-Methylhexane (racemic mixture)			2,2-Dimethylpentane			3,3-Dimethylpentane			2,4-Dimethylpentane			2,3-Dimethylpentane			2,2,3-Trimethylbutane					
<i>t</i> °C.	<i>T</i> °K.	$\frac{\Delta F_T^\circ}{T}$	<i>K</i>	<i>N</i>	$\frac{\Delta F_T^\circ}{T}$	<i>K</i>	<i>N</i>	$\frac{\Delta F_T^\circ}{T}$	<i>K</i>	<i>N</i>	$\frac{\Delta F_T^\circ}{T}$	<i>K</i>	<i>N</i>	$\frac{\Delta F_T^\circ}{T}$	<i>K</i>	<i>N</i>	$\frac{\Delta F_T^\circ}{T}$	<i>K</i>	<i>N</i>	$\frac{\Delta F_T^\circ}{T}$	<i>K</i>	<i>N</i>	$\frac{\Delta F_T^\circ}{T}$	<i>K</i>	<i>N</i>	$\frac{\Delta F_T^\circ}{T}$	<i>K</i>	<i>N</i>
25	298	0	1	0.009	-4.01	7.52	0.068	-3.62	6.18	0.056	-6.99	33.7	0.30	-6.75	29.9	0.27	-4.57	9.98	0.090	-4.80	11.2	0.100	-4.85	11.5	0.103			
127	400	0	1	0.032	-2.59	3.68	0.12	-2.69	3.87	0.13	-3.09	4.73	0.15	-4.49	9.57	0.31	-1.79	2.46	0.079	-2.29	3.16	0.102	-1.47	2.09	0.068			
227	500	0	1	0.062	-1.74	2.40	0.15	-2.14	2.94	0.18	-0.84	1.53	0.10	-3.08	4.71	0.29	-0.18	1.09	0.068	-0.62	1.37	0.085	0.60	0.74	0.046			
327	600	0	1	0.092	-1.13	1.77	0.16	-1.70	2.36	0.22	0.60	0.74	0.068	-2.10	2.88	0.27	1.00	0.60	0.056	0.44	0.80	0.074	1.92	0.38	0.035			
527	800	0	1	0.14	-0.42	1.24	0.17	-1.22	1.85	0.26	2.33	0.31	0.044	-0.87	1.55	0.22	2.38	0.30	0.043	1.68	0.43	0.061	3.49	0.17	0.024			
727	1000	0	1	0.17	-0.12	1.06	0.18	-1.02	1.67	0.29	3.28	0.19	0.033	-0.14	1.07	0.18	3.06	0.21	0.037	2.34	0.31	0.053	4.35	0.11	0.019			

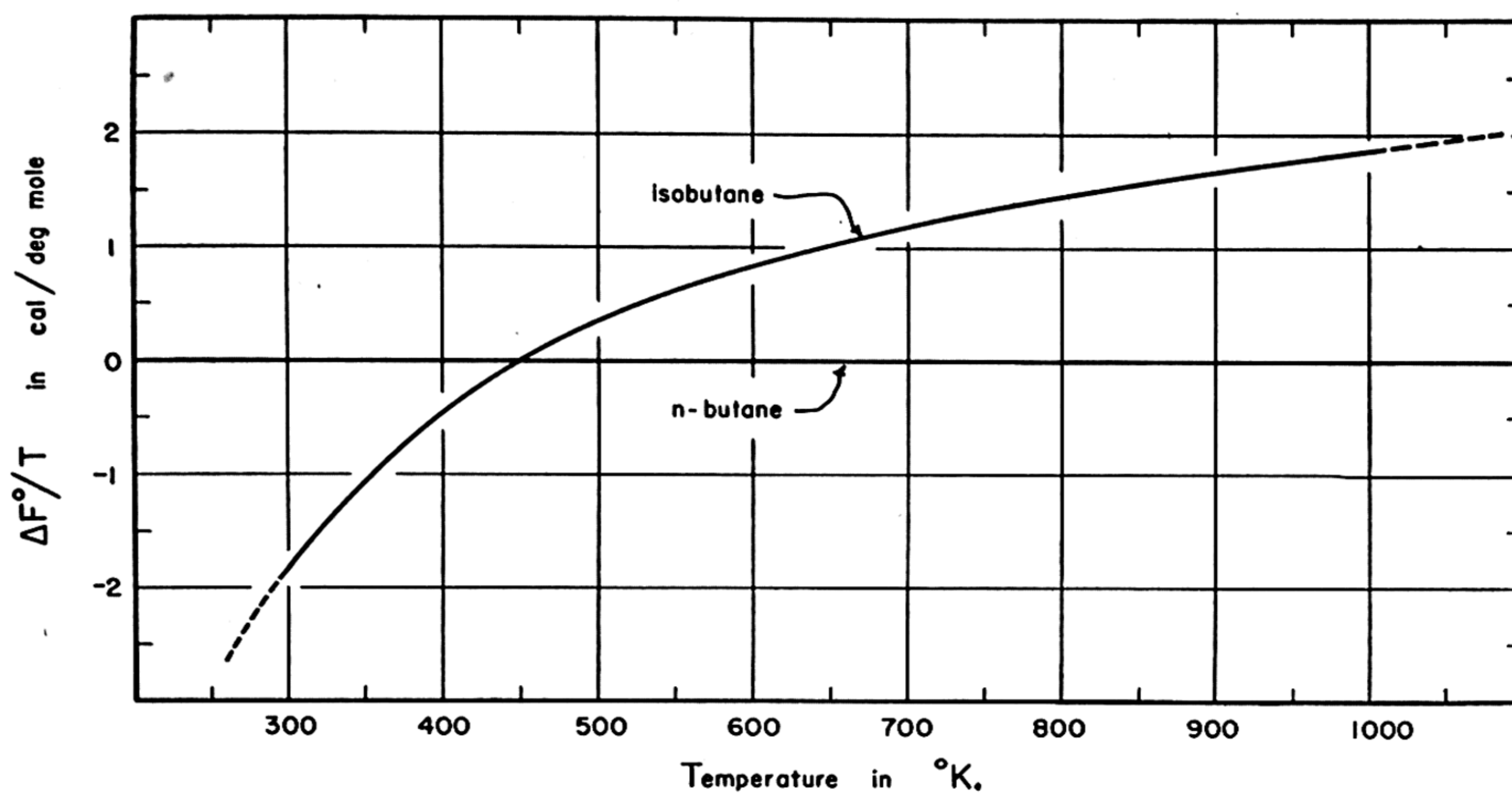


FIG. 1.

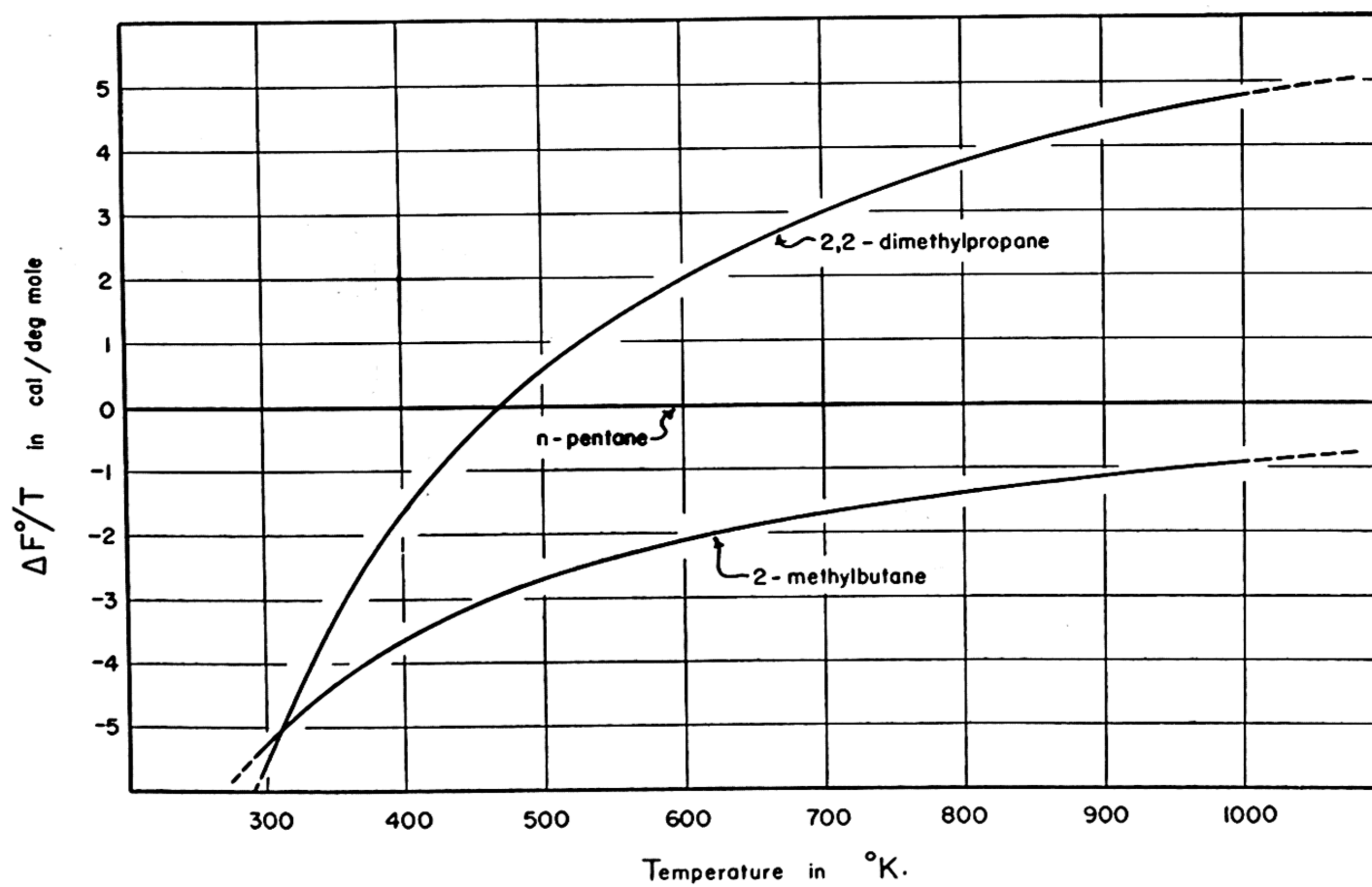


FIG. 2.

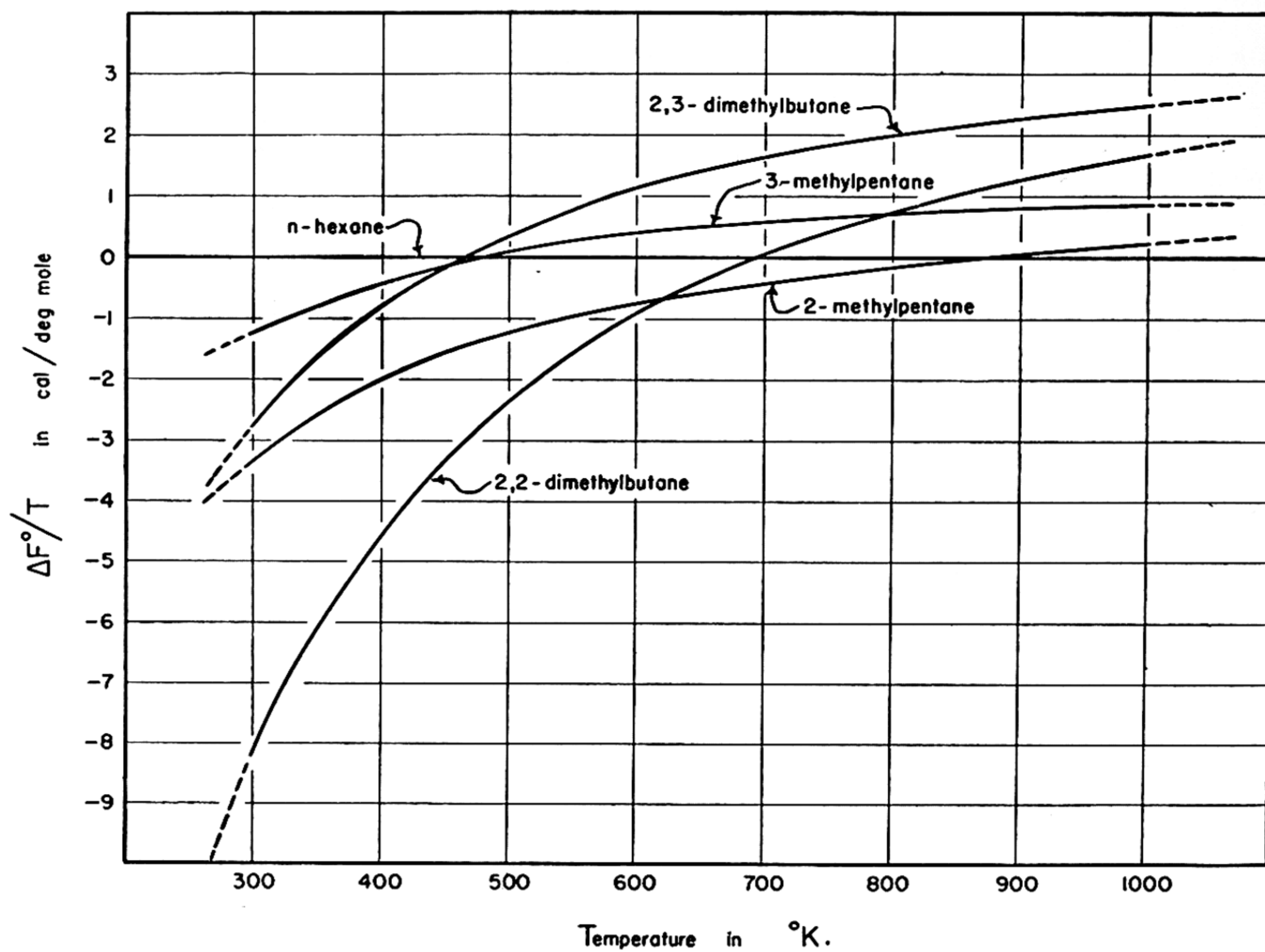


FIG. 3.

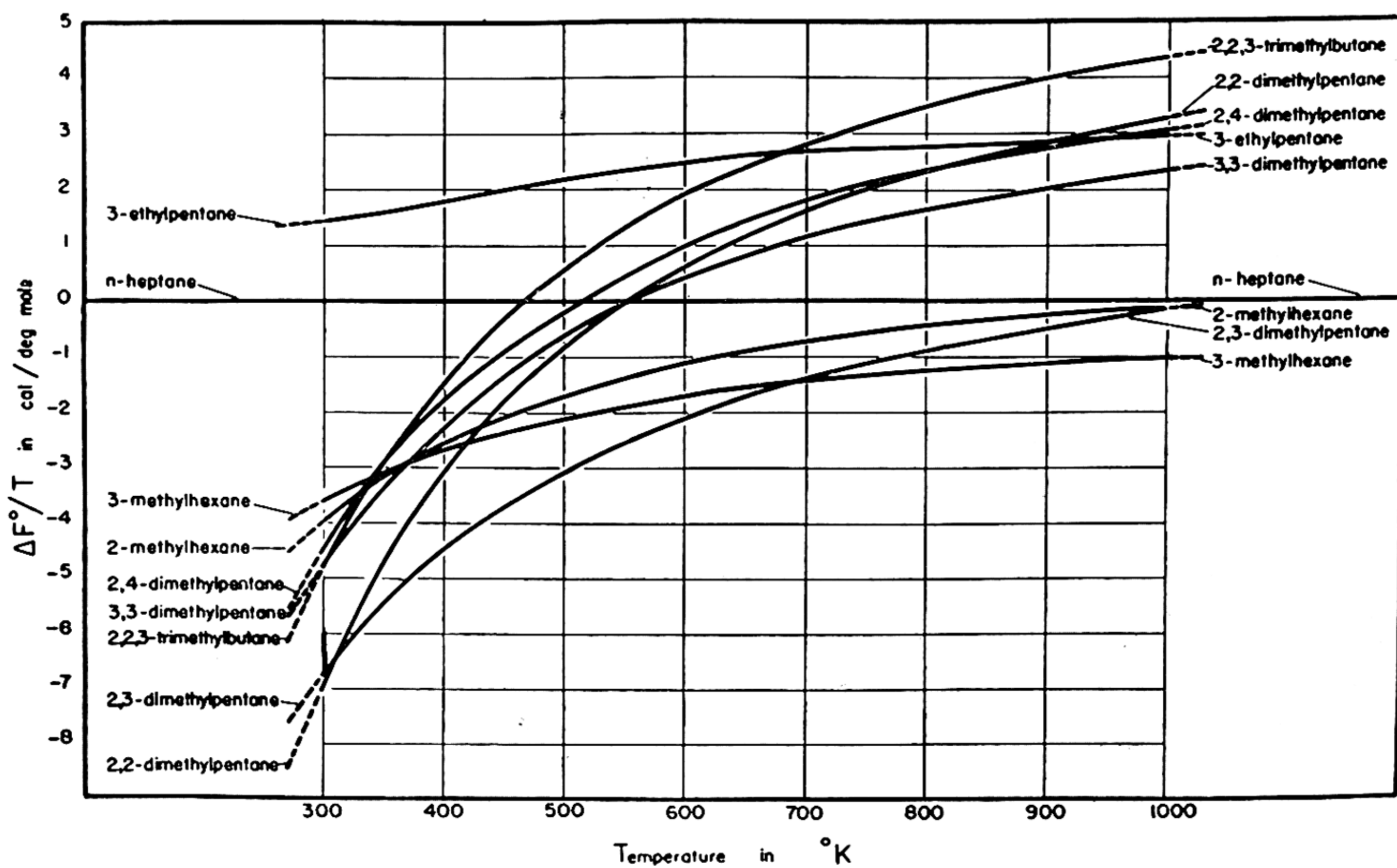


FIG. 4.

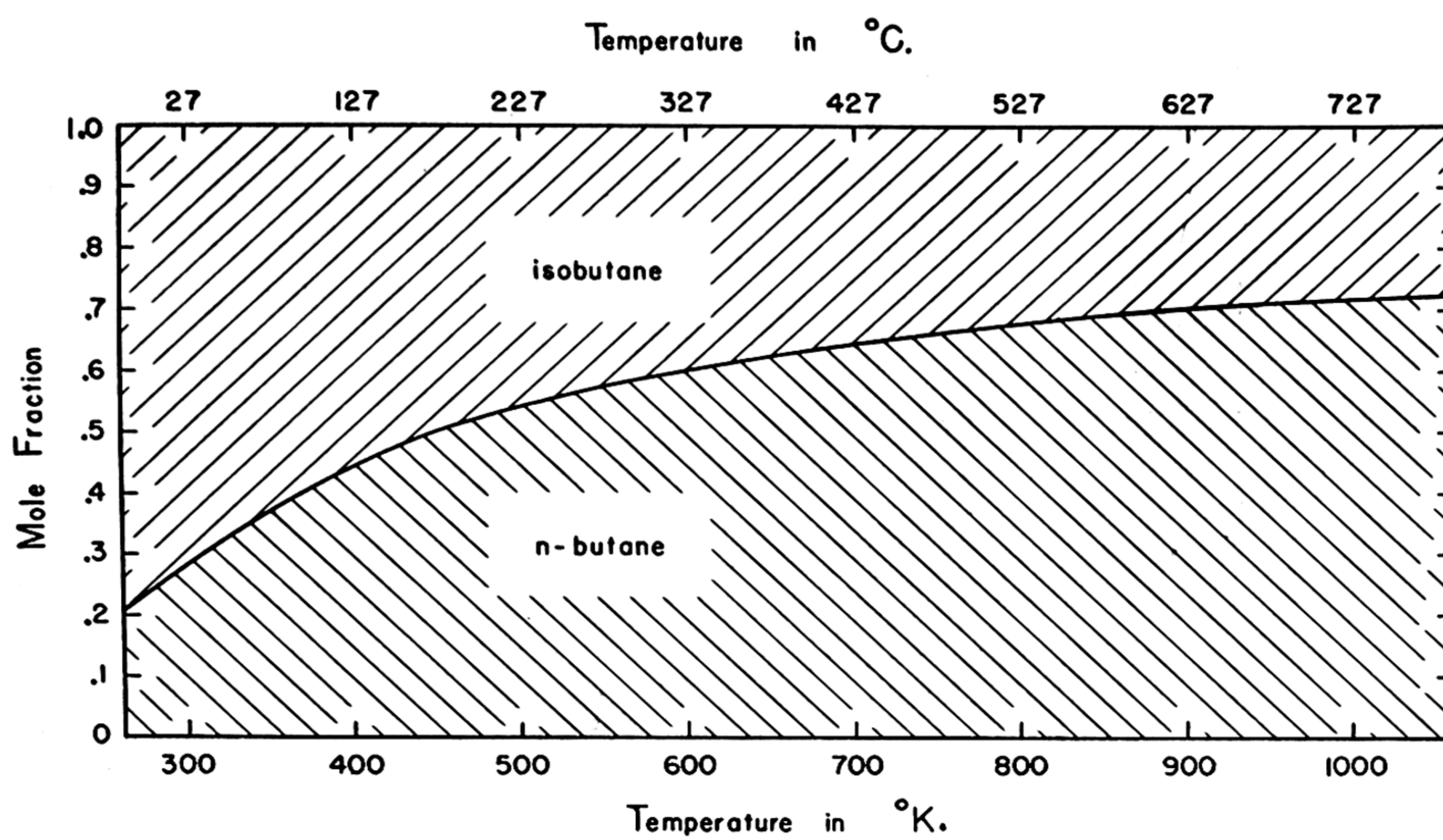


FIG. 5.

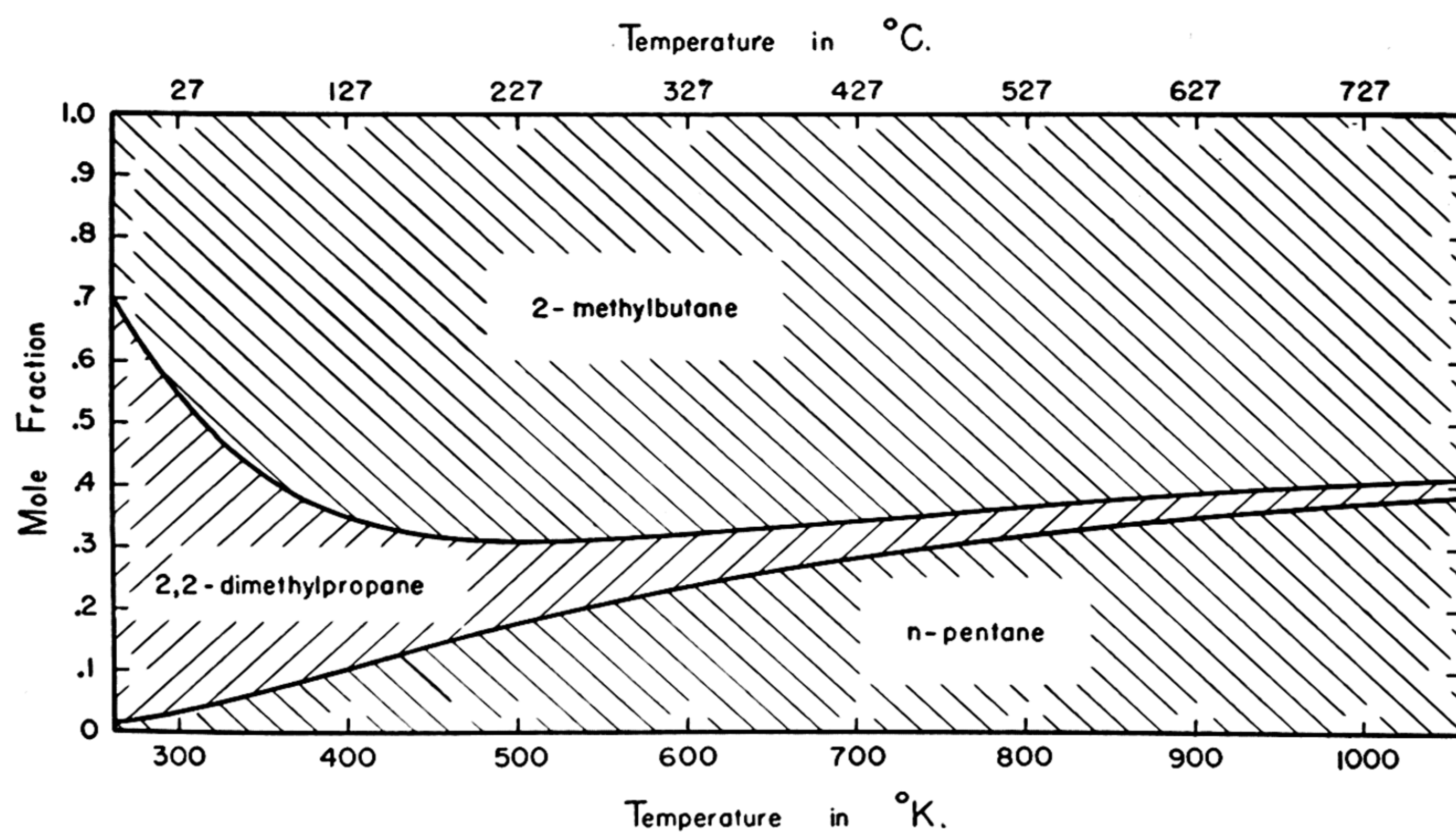


FIG. 6.

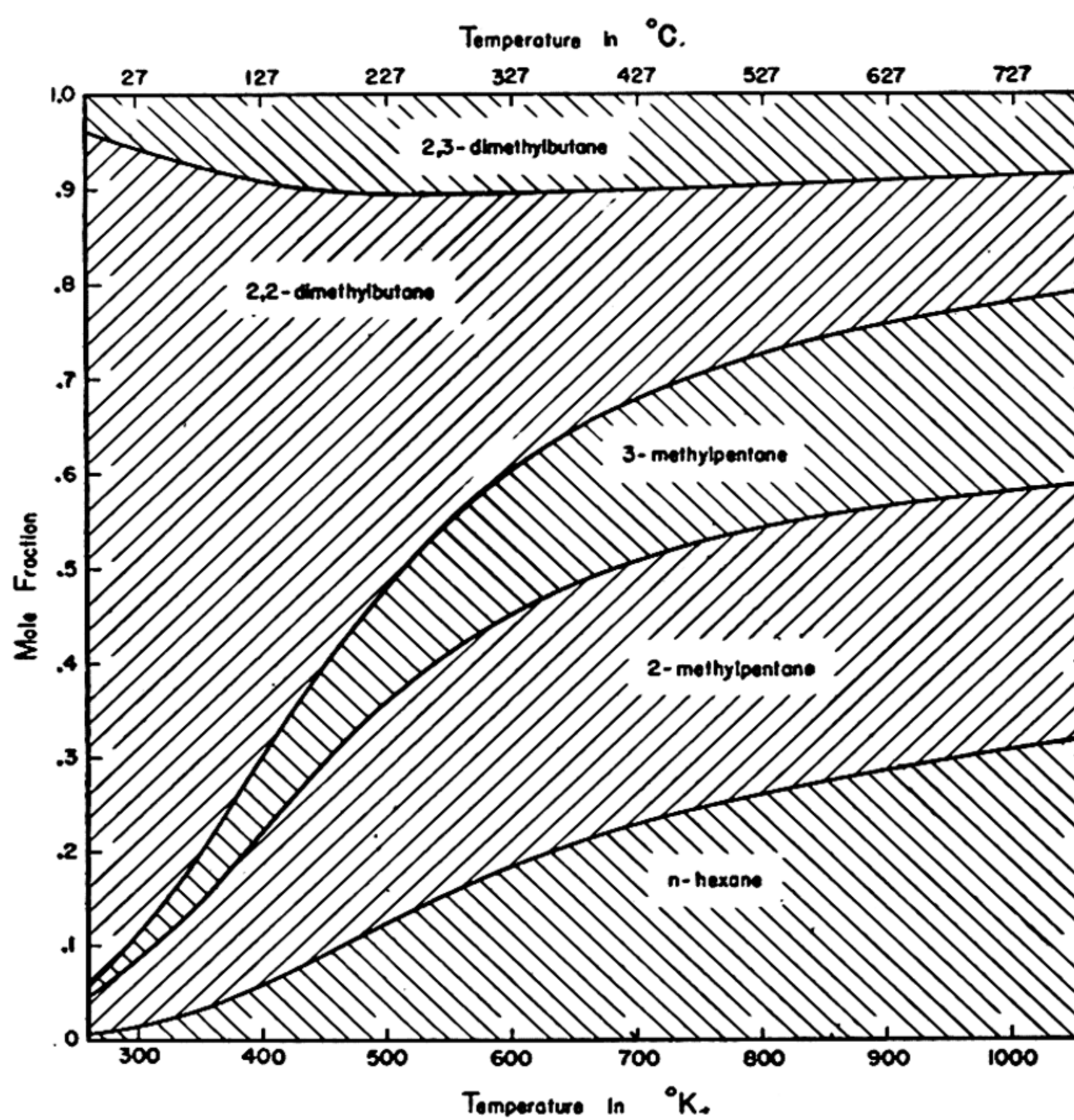


FIG. 7.

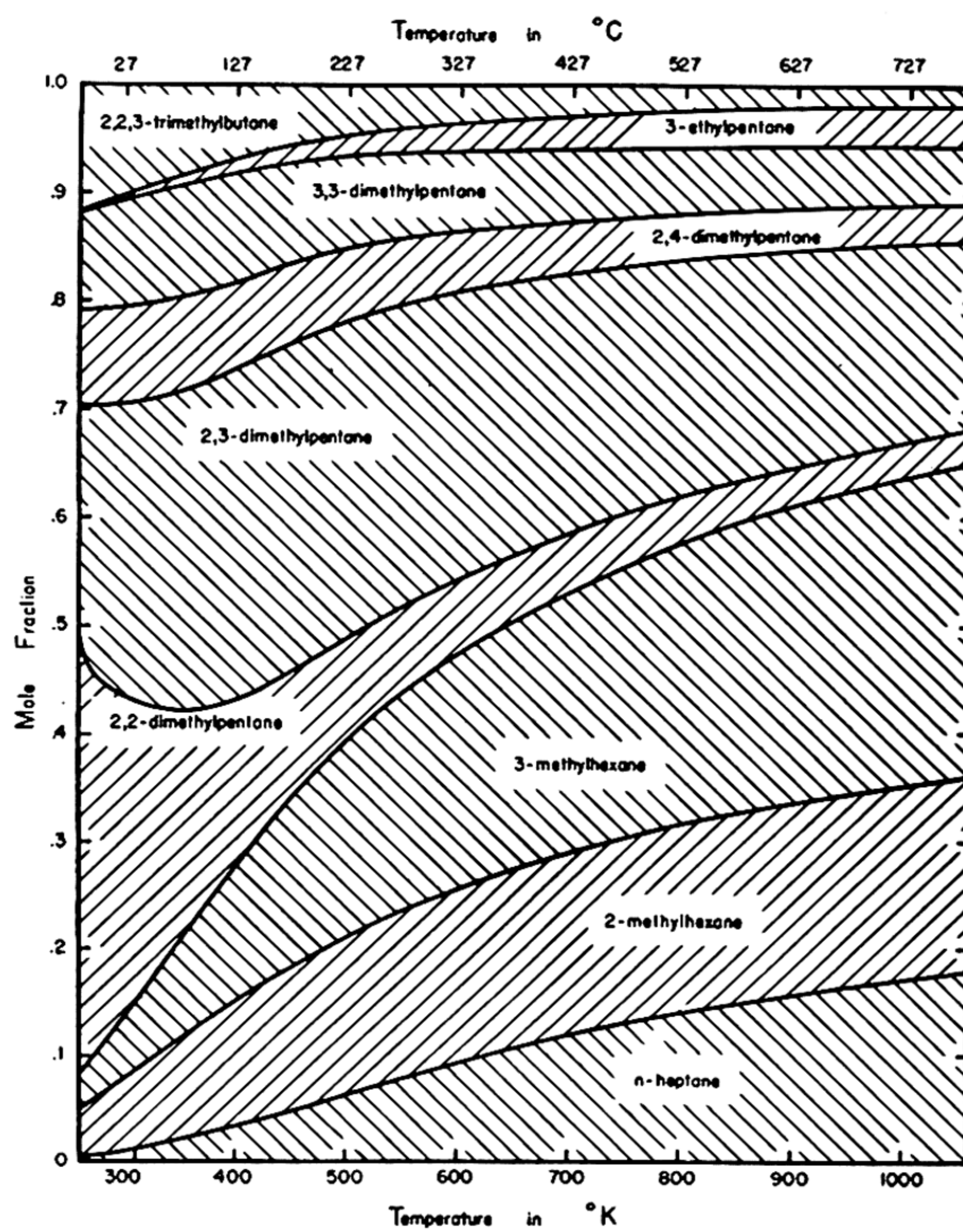


FIG. 8.

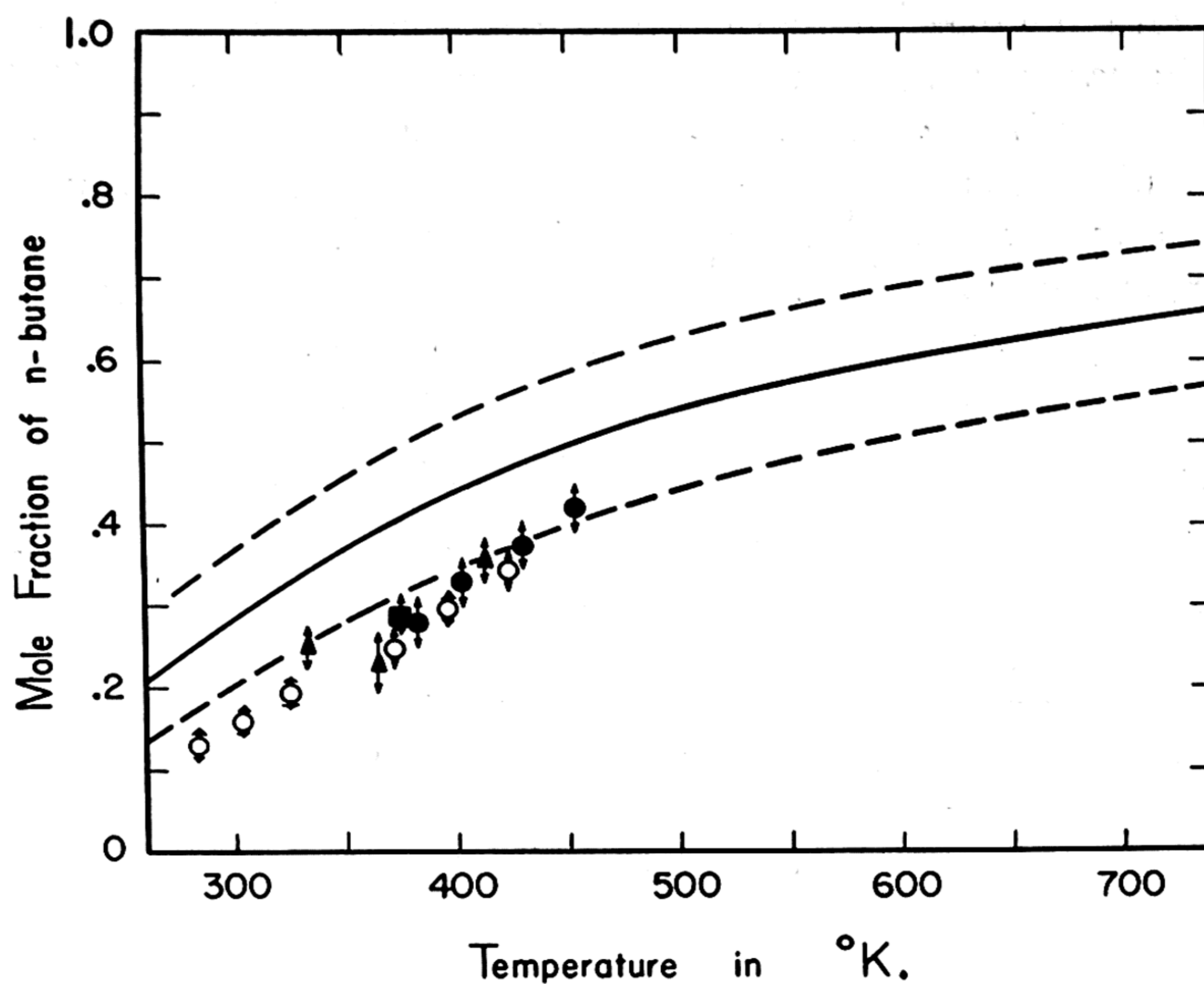


FIG. 9.

- = Montgomery, McAteer, and Franke.^{384, 385} Also Thorne.^{477b}
 ● = Moldavsky and Nisovkina.³⁸²
 ▲ = Schuit, Hoog, and Verheus.^{529a}
 ■ = De Simo, McMillan, and Cheney.^{135a}

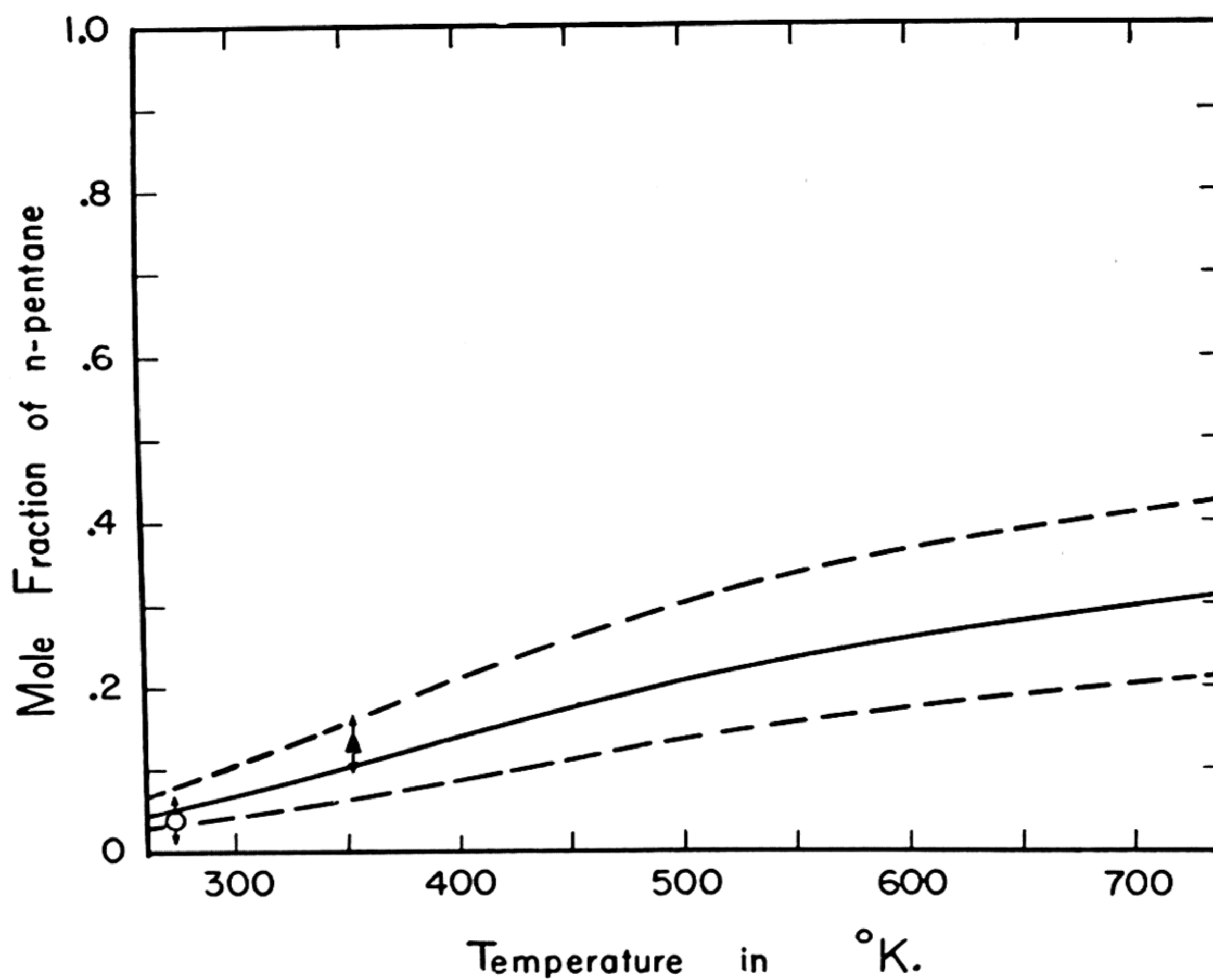


FIG. 10.

stability with increase in temperature, over the range 298 to 1000° K., and, at the latter temperature, is among the most stable of the isomers.

“(c) At 25° C., the 2,2-dimethyl isomer is in each case the most stable, but it rapidly becomes less stable with increasing temperature and at 1000° K. is among the least stable of the isomers.”

The experimental data on all known isomerizations of alkanes, occurring in the presence of aluminum halides and other catalysts, are presented in Table 6, p. 218.

Conclusions

(1) Catalytic isomerization of alkanes proceeds by a change in the molecular configuration such that methyl groups are apparently transferred.

(2) Aluminum halides are, to date, the most effective catalysts for isomerization of alkanes.

(3) Isomerization of alkanes is generally accompanied by the formation of hydrocarbons with lower and higher carbon contents.

Chapter II

Alkenes, Alkadienes, and Alkapolyenes

The aliphatic hydrocarbons with double bonds to be discussed in this chapter are: alkenes, allenic alkadienes, non-allenic alkadienes, and alkapolyenes (cyclenes will be considered in Chapter V).

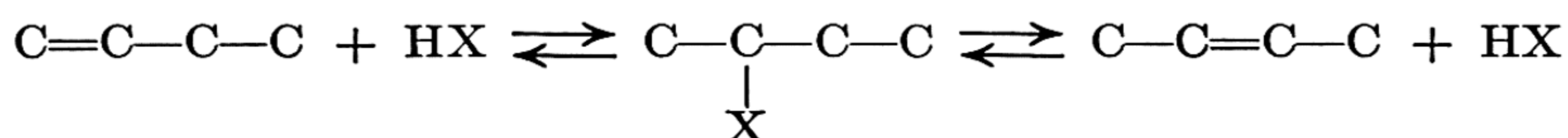
ISOMERIZATION OF ALKENES

Mechanism

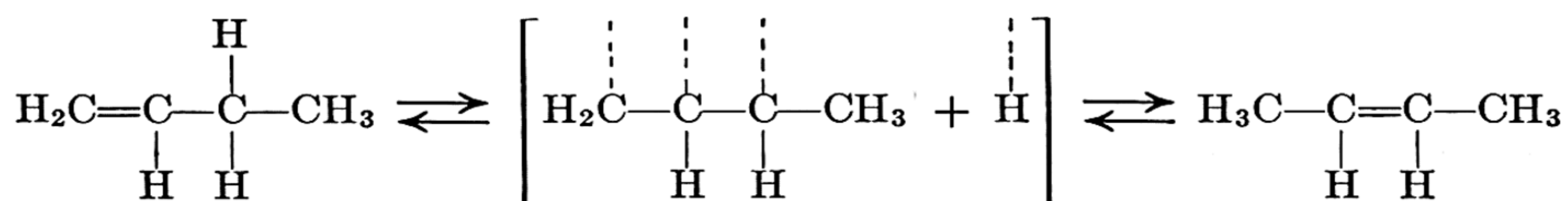
Isomerization of alkenes may proceed in several directions:

1. **Isomerization by shift of a double bond.** This change occurs theoretically in one or more ways, *e.g.*,

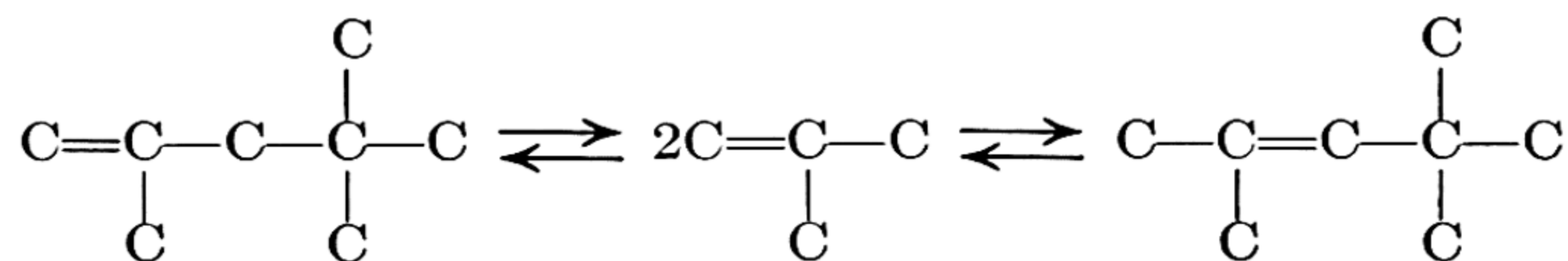
(a) by the formation of an unstable intermediate product:



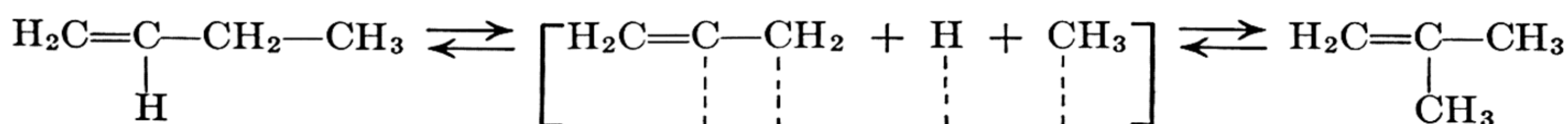
(b) by the occurrence of free radical processes (the broken lines represent residual valences assignable to the radicals):



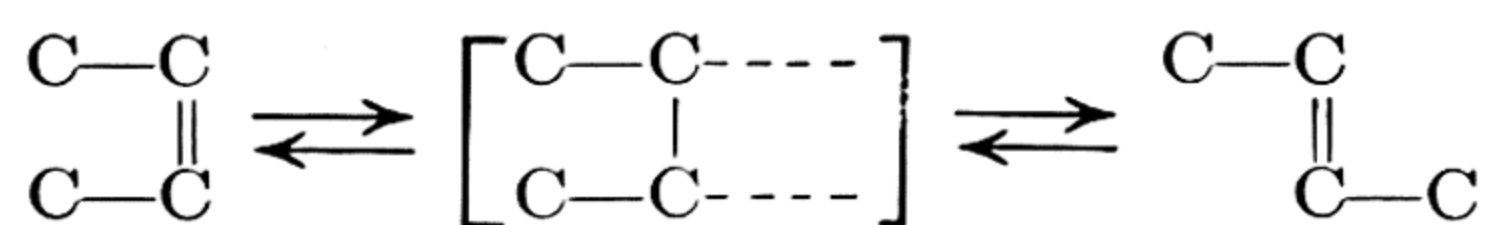
(c) by depolymerization plus polymerization (both hypothetical reactions):



2. **Isomerization by change in chain branching alone.** This occurs theoretically through a free radical exchange, *e.g.*,



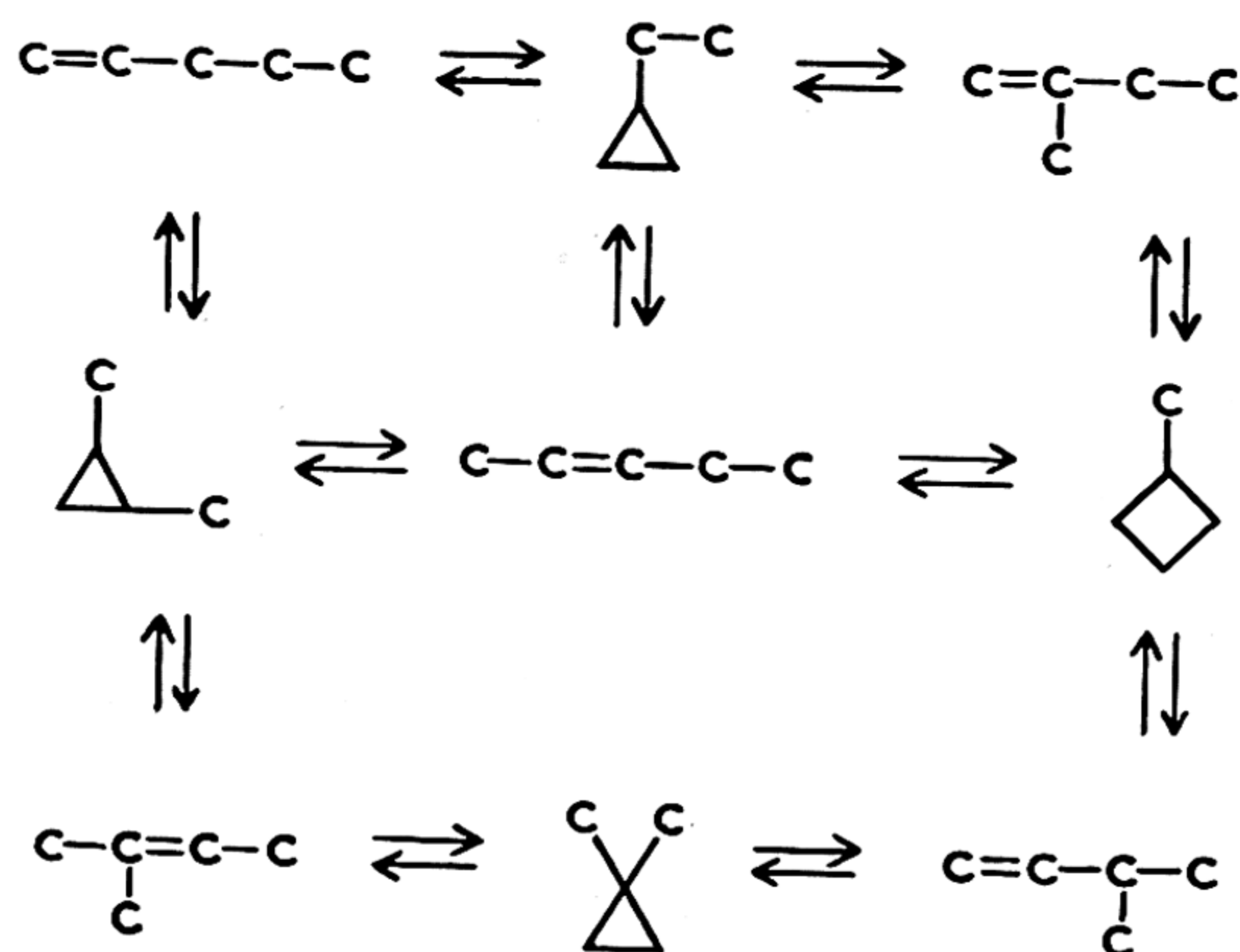
3. **Isomerization by interconversion of cis and trans isomers, *e.g.*,**



4. Isomerization by cyclization, or "internal" alkylation. This results in the formation of a cyclane, *e.g.*,

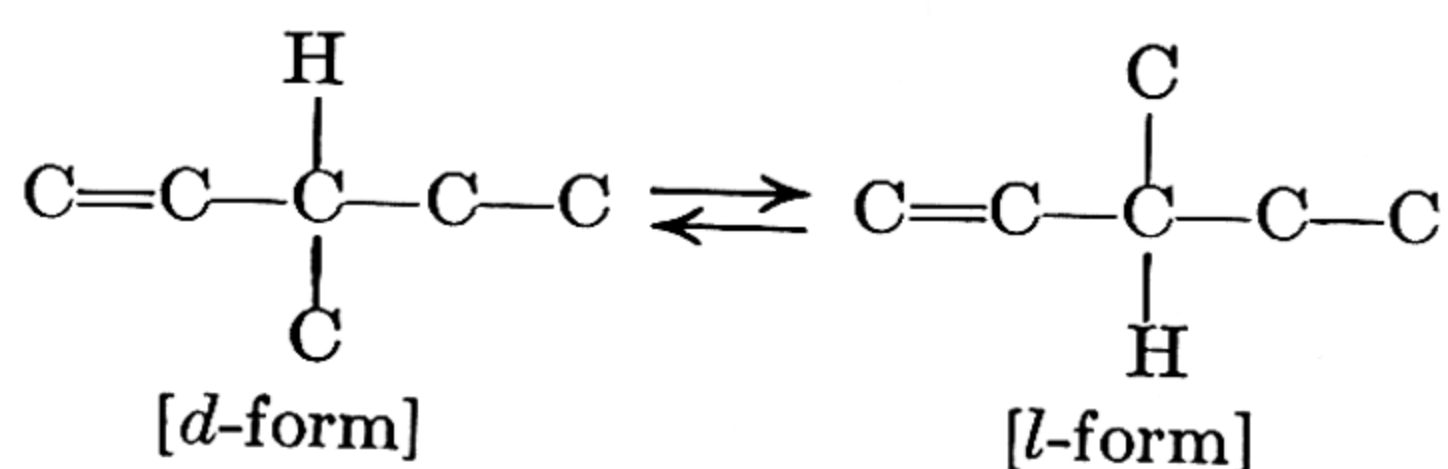


5. Isomerization by hydrogen transfer plus cyclization, followed by decyclization plus hydrogen transfer. The isomers are formed by variable branching and cyclization, *e.g.*,



6. Isomerization by polymerization plus intermediary isomerization of the polymer plus depolymerization. This sequence of reactions seems quite probable, but has not been studied to date.

7. Isomerization by change in arrangement of the 4 different groups about an asymmetrical carbon atom. The following case would be the simplest.



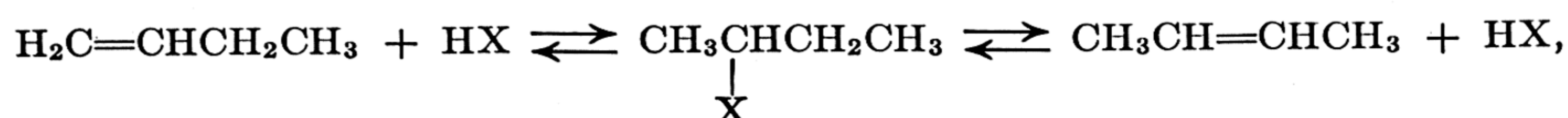
Isomerization of the alkenes, proceeding in any of the first 6 preceding directions, requires a shift of the hydrogen atom (except in those rare and as yet unstudied cases where such hydrogen is replaced by an alkyl). Formation of isomers according to directions 2, 5, and 6 requires the "rupture" of a C—C bond as well. This occurs either in the manner of isomerization of alkanes or by the formation of a short-lived cyclane.

It may be pointed out that whenever a transfer of a hydrogen atom takes place, resulting in the shift of a double bond, a three-carbon or allylic-type isomerization is apparently involved. This process may be

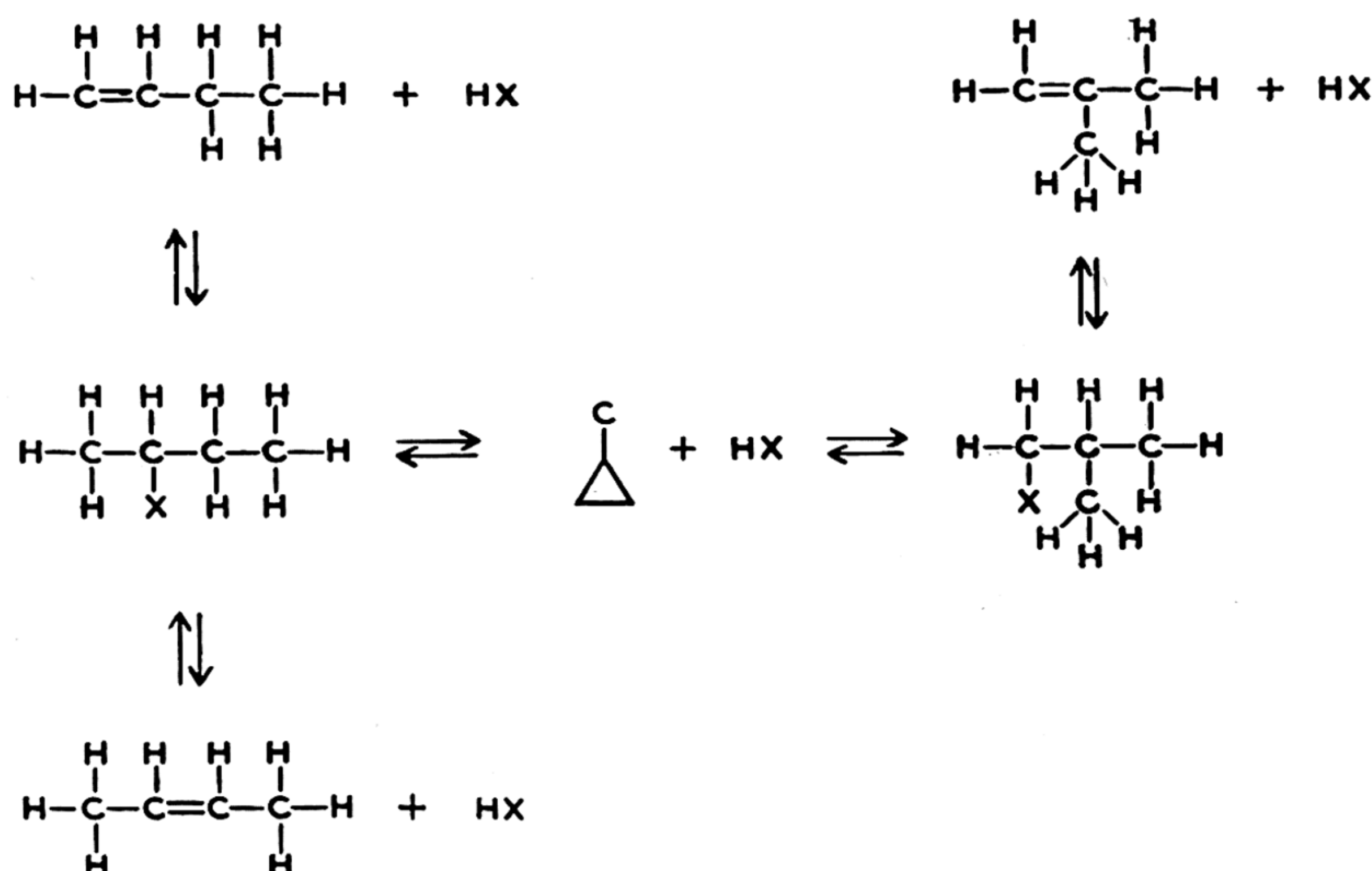
repeated if the molecule is a long one. The mechanism of an acid-catalyzed double-bond shift consists of 2 steps:²⁸⁵

(1) Formation of an addition product from the alkene and the catalyst, and

(2) Decomposition of the addition product, whereby the same alkene or one with a different structure is split off, and the catalyst regenerated. The reaction can be formulated as follows:²⁸⁵



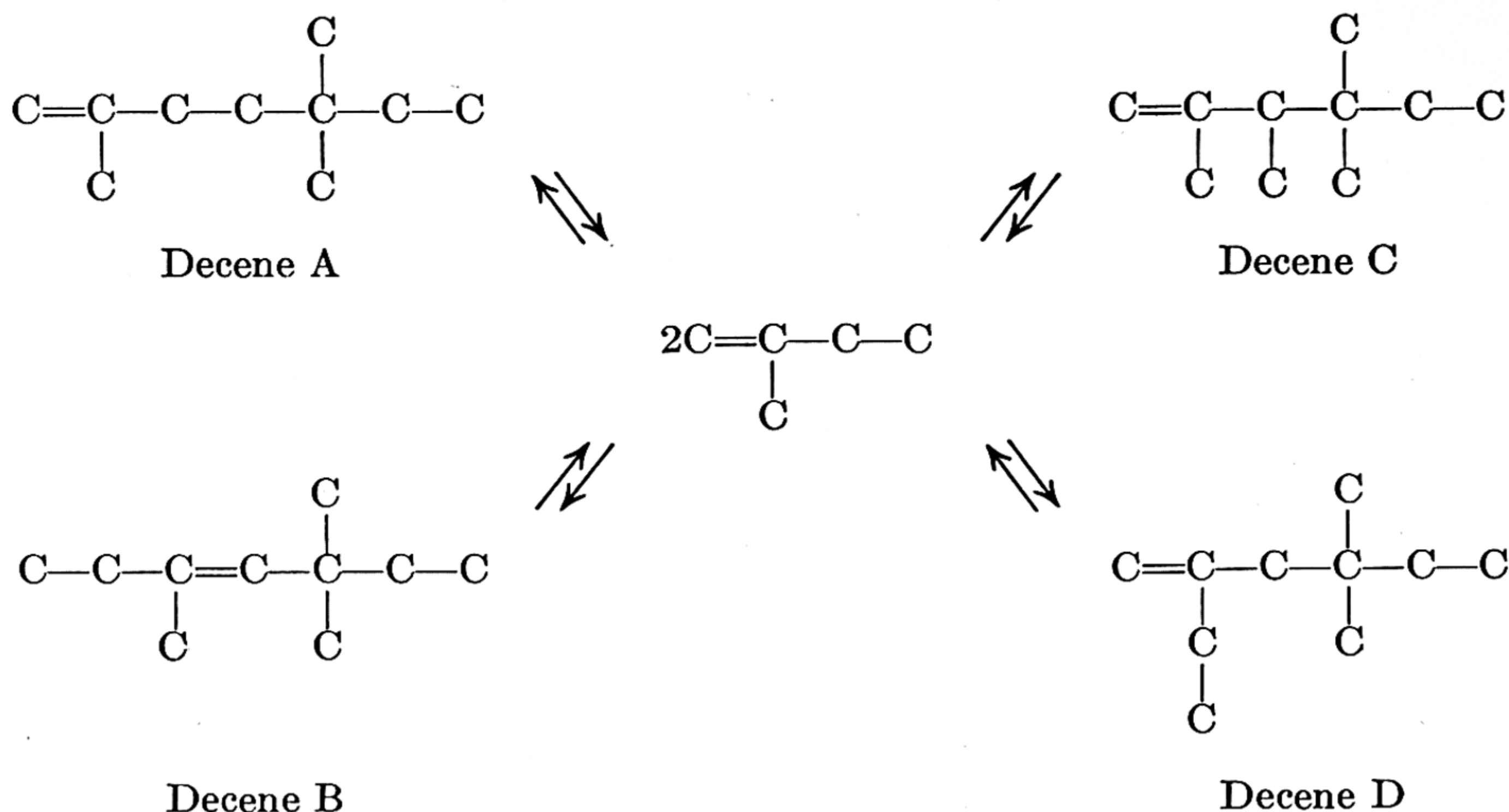
where "X" represents a negative group. This mechanism can be used for the interpretation of the isomerizations involving a short-lived cyclane or yielding a stable one. This requires the preliminary removal of hydrogen from a carbon atom which is more remote to the "X" group, *e.g.*:



The postulated cyclizations are actually intramolecular alkylations in which part of the molecule is alkylated either by a condensation within an ester or through the addition upon the double bond (direction 5). The conversion of a short-lived cyclane into its isomers may proceed without the catalyst, HX, by an alternative thermal isomerization. In all these cases the decyclization of a short-lived cyclane is the reverse process of "dealkylation" into an alkene.

Isomerization of alkenes by change of carbon-chain configuration (direction 2) may be at times the result of a destructive alkylation, or depolymerization plus polymerization (direction 1c). Thus, depolymerization of any of the following decenes A, B, C, or D into 2-methyl-

butene-1, followed by polymerization, should lead largely to isomer formation with a change in branching:



The mechanism of alkene isomerization in still other cases may approach that of the alkanes, especially when changes occur in those parts of the alkene molecule remote from the double bond.

The alkenes are characterized by a tendency to polymerize, which must be taken into account in isomerization processes. The conditions of isomerization and the catalysts applied are preferably mild, in order to avoid formation of polymers. Furthermore, the temperatures used in

Table 7. Number of Structurally Isomeric Hydrocarbons of the Alkene Series.
(Excluding the additional isomers due to stereoisomerism)

*From Henze and Blair*²⁴⁸

Carbon content	Number of isomers
2	1
3	1
4	3
5	5
6	13
7	27
8	66
9	153
10	377
11	914
12	2,281
13	5,690
14	14,497
15	36,564
16	93,650
17	240,916
18	623,338
19	1,619,346
20	4,224,993

Note: The correct number of $\text{C}_{14}\text{H}_{28}$ isomers is 14,397, according to Henze and Blair.²⁴⁹

catalytic isomerization are close to those in cracking and polymerization.⁴³⁷ In reactions carried out with strong catalysts (*e.g.*, aluminum halides), as well as at high temperature, very little isomerization takes place. It is then accompanied or succeeded by other reactions (*e.g.*, polymerization, hydrogen disproportionation, and alkylation).

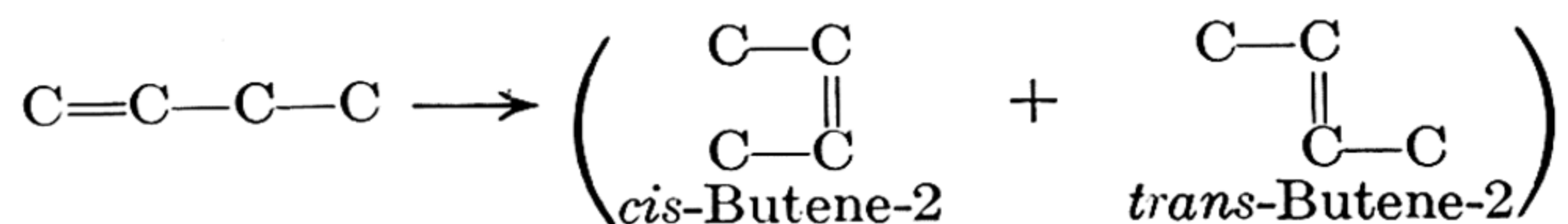
Identification of the alkene isomers is facilitated by their chemical activity, as contrasted to the alkanes. A suitable method of identification of *cis-trans* alkene isomers is a simple reaction-rate measurement using alkene dibromides and potassium iodide.⁶⁵⁸ The *cis* and *trans* forms of butene-2 have widely different coefficients of thermal conductivity; these isomers, therefore, may be analyzed by means of the Pirani gauge.^{600a} The number of structurally isomeric alkenes (Table 7) greatly exceeds that of the alkanes with the same content of carbon atoms per molecule.

Isomerizations

Propene. The conversion of cyclopropane into propene is a well-established fact. However, the isomerization of propene by cyclization to cyclopropane has been reported only twice: (1) the heating of propene at 400-405°, whereby more than 50 per cent of a product containing cyclopropane was obtained,¹⁶⁶ and (2) the formation of about 60 per cent of cyclopropane from propene at 410°.²⁰³ Some workers cast grave suspicions on this observation by pointing out the highly-strained condition of cyclopropane and the consequent unfavorable equilibrium states.⁵⁹⁰



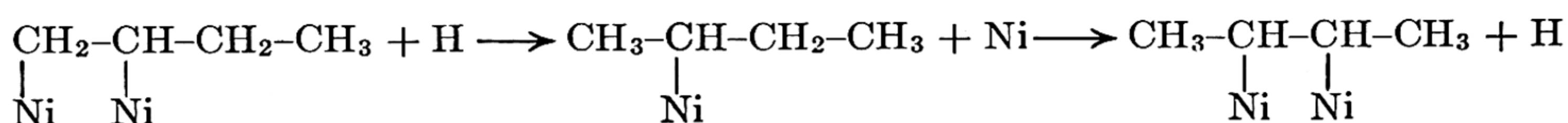
Butenes. Butene-1, passed through a quartz tube at 550°, gave butene-2 (87 per cent) without formation of isobutene.^{266,267} In another case, butene-1 at 650° gave a butene *fraction* containing high-boiling butene-2 (8 per cent), low-boiling butene-2 (13 per cent), and butene-1 (79 per cent).²⁶⁴ Hence, butene-2 is formed in the proportion of 38 per cent of the *cis* form (high-boiling, reported incorrectly as *trans*) to 62 per cent of the *trans* form. At 700° the butene fraction has 16 per cent of butene-2 and 84 per cent of butene-1. Isobutene was absent in all cases.²⁶⁴



Various catalysts²⁸⁵ permit the conversion of butene-1 into butene-2 at much lower temperatures. Solutions of zinc chloride (75 per cent at 100°), benzenesulfonic acid (75 per cent at 76°), and perchloric acid (71 per cent at 21°) gave 5, 13, and 21 per cent of butene-2 at atmospheric pressure, respectively. Pure phosphoric acid at atmospheric pressure con-

verted butene-1 into butene-2 to the extent of 12 per cent at 78° and 60 per cent at 135°. Phosphoric acid, on diatomaceous earth, catalyzed a complete conversion of butene-1 to butene-2 at 249° and 7.8 atmospheres' pressure. The reaction efficiency decreases upon lowering the temperature.

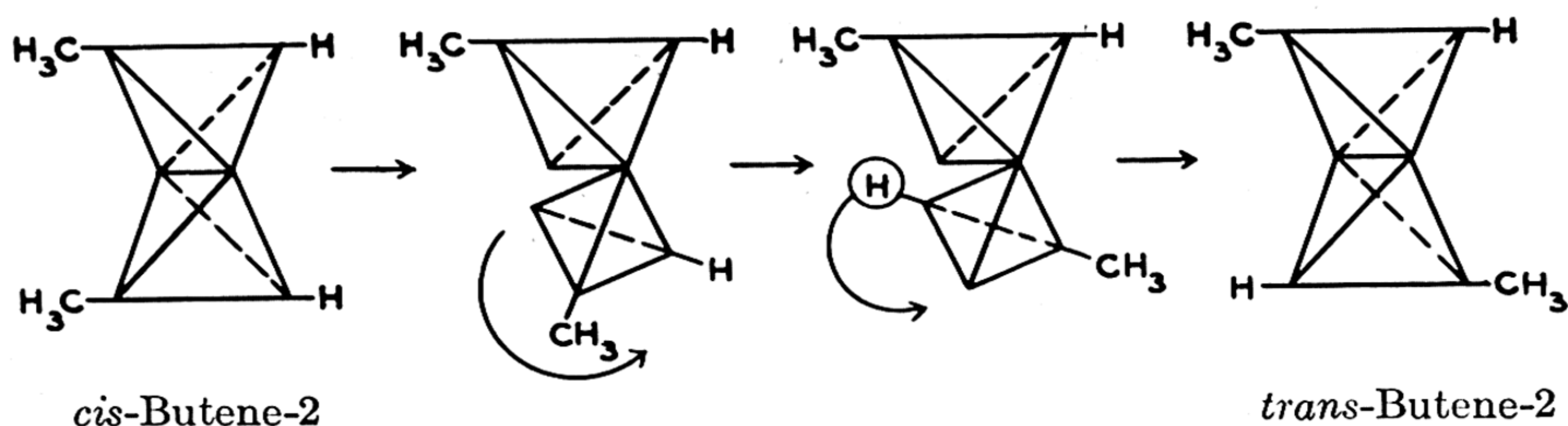
Isomerization of butene-1, within lime-filled porcelain tubes, at 420° yields 92 per cent of butene-2.^{266, 267} Catalysts, such as bauxite, silica, titania, difficultly-reducible metal oxides, neutral borates, neutral phosphates, neutral silicates, and aluminum phosphate on pumice acted similarly at 400°.^{266, 267} Aluminum sulfate was found to be effective also.²¹² An isomerization of butene-1 into butene-2 occurs in the dehydration of butanol-1 over alumina and is probably due either to the catalytic action of traces of sulfuric acid³⁶² or to an accumulation on the catalyst of acidic materials resulting from oxidation (by traces of air introduced into the catalyst chamber during shut-down periods).²⁸⁵ Butene-1 probably isomerizes to butene-2 upon interaction with an equal amount of hydrogen at 133° in the presence of nickel.⁶⁰⁰ The formation of butene-2 was indicated only by a decrease in the vapor pressure of the product. The reaction does not occur in the absence of hydrogen and gives simultaneously 10 per cent of *n*-butane. Subsequent work indicates that the isomerization of butene-1 into butene-2 in the presence of hydrogen and fine nickel wire at 65° is reversible and proportional both to the square root of the total pressure of the butenes and to the square root of the hydrogen pressure.^{600a} The equilibrium concentration of butene-2, approached from both sides at 65°, was found to be about 93 per cent of the total concentration of butenes. No isomerization occurred at 65° when hydrogen was absent in the initial butene-1, even though nickel was present. The following "associative mechanism" was proposed for the isomerization of butene-1:



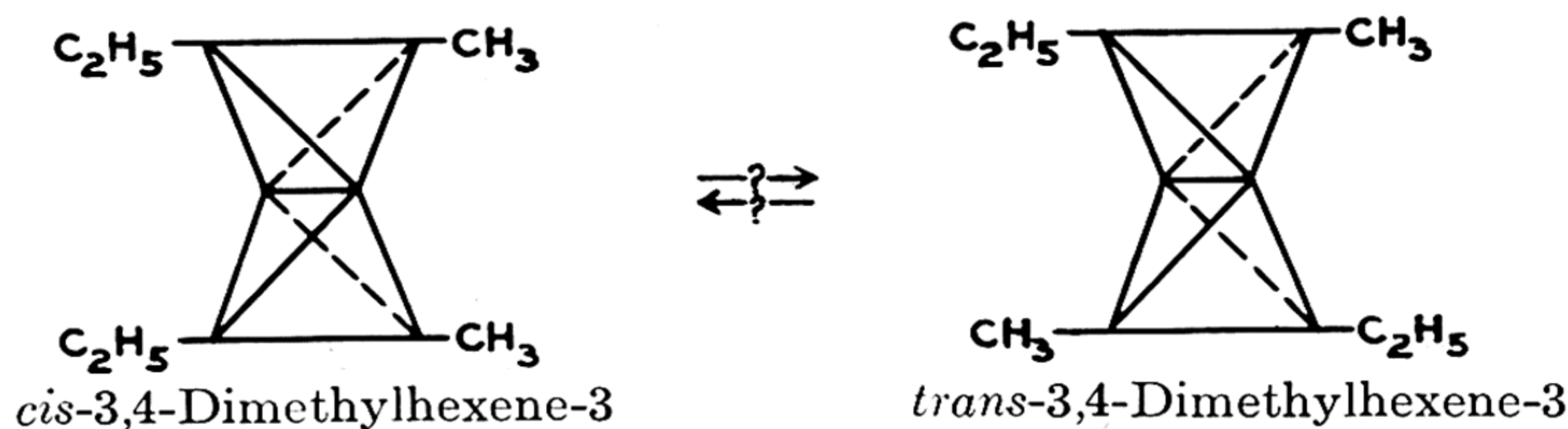
The activation energy for the double-bond migration was given as 5.9 kilocalories per gram-mole of butene-2 formed at 76-126°.^{600a}

The isomerization of butene-2 is of special interest because of the existence of 2 forms, *cis* and *trans*, in this hydrocarbon. These forms occur because of two possible stereochemical arrangements of the terminal methyl radicals about an ethylene group. The methods of preparation, physical constants,¹⁵³ properties, electron diffraction measurements,⁹² ultraviolet absorption spectra,⁹⁹ heat of hydrogenation,³⁰⁵ and isomerization and addition reactions^{581c} of butene-2, have jointly established the facts that the low-boiling butene-2 is the *trans* form and that the *cis-trans* isomerization is characteristic of certain alkenes.

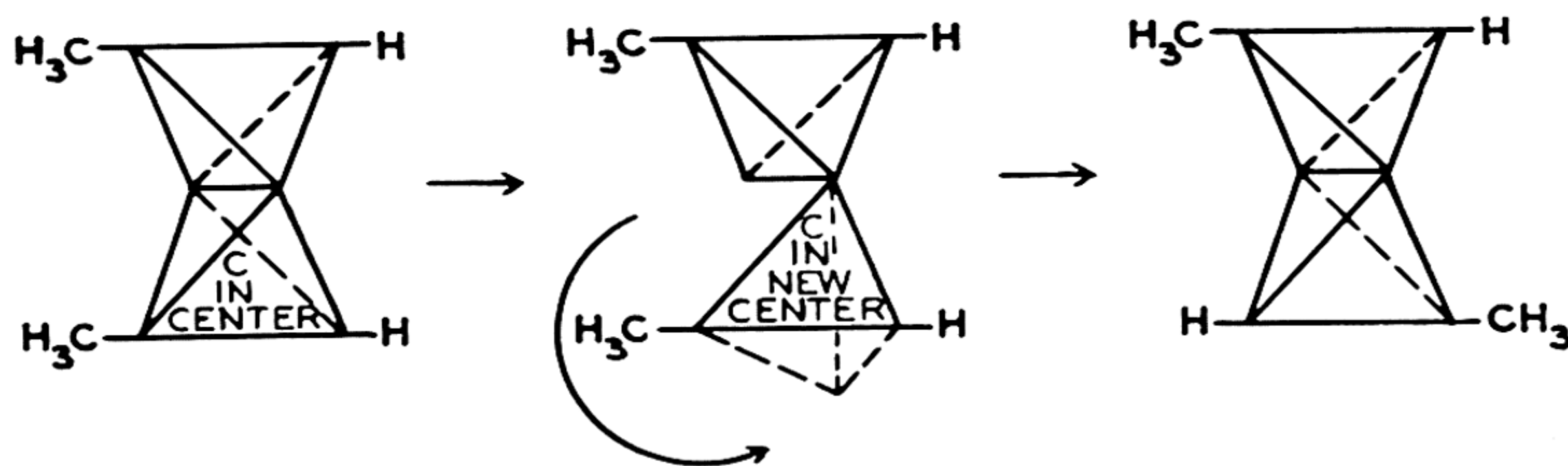
The isomerization of *cis*- into *trans*-butene-2 and of *cis*- into *trans*-pentene-2 probably involves a transfer of hydrogen with the "opening and closing" of the double bond. Such a mechanism seems to be more plausible than the exchange of a hydrogen atom and an alkyl group. From this point of view, there cannot be a complete C—C break and a reunion in the isomerization of butene-2 and of pentene-2, but there is rather a *partial break* followed by a *rotation*:



On account of this mechanism, the question arises whether it is possible to have a *cis-trans* isomerization of tetra-alkyl ethylenes, wherein no labile hydrogen occurs about the double bond, as in the case of *cis*-3,4-dimethylhexene-3:



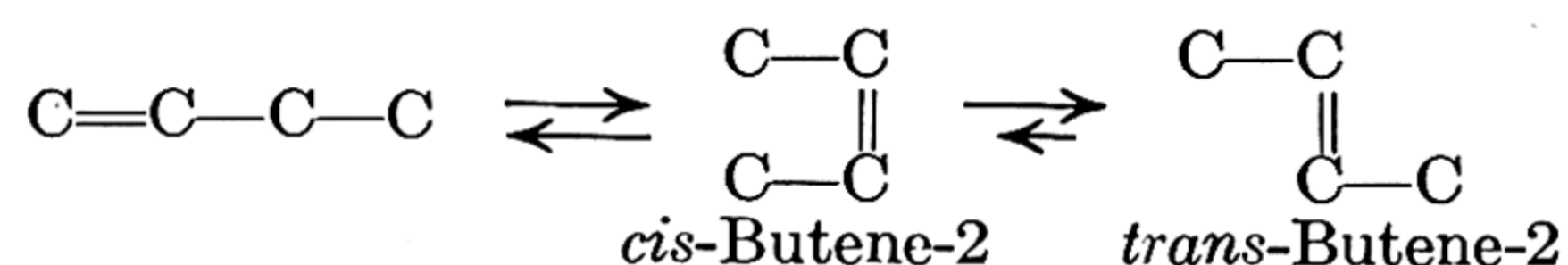
An alternative explanation of the isomerization of *cis*- into *trans*-butene-2 involves a 180° redistribution of the electronic charge about one particular carbon atom (actively involved in the "opening" of the double bond). This carbon atom forms the basis of a "new tetrahedron," and is followed by a 180° rotation. In this case, a labile hydrogen atom or labile alkyl group would be unnecessary.



The idea of a "new tetrahedron" is used in organic chemistry to explain such reactions as the Walden inversion³⁵⁰ and the photochemical isomerization of *cis*-cinnamic acids.⁶⁴

The *cis-trans* isomerization of butene-2 has an equilibrium constant near 1.12 at 390°, corresponding to 52.8 per cent of the *trans* isomer.³⁰⁷ A study of kinetics in the conversion of *cis*- into *trans*-butene-2 at 390-420° has indicated a homogeneous reaction of approximately first order.³⁰⁷ However, it has been pointed out that a bimolecular mechanism is equally justifiable as an interpretation of the data.²⁴¹

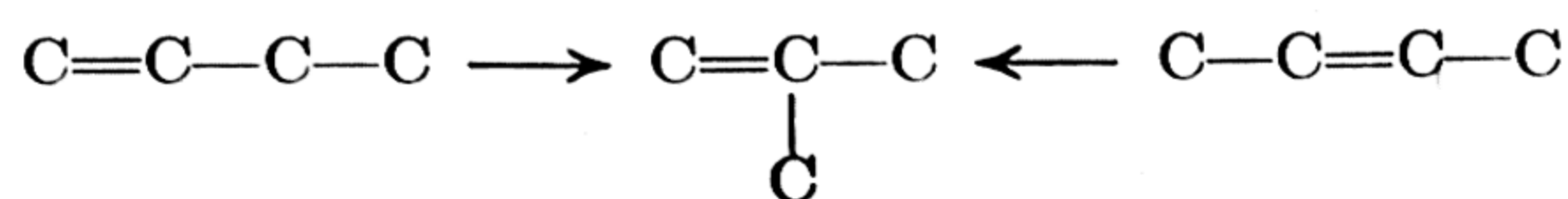
A mixture of 38 per cent high-boiling (*cis*) and 62 per cent low-boiling (*trans*) butene-2, heated at 650° and 700°, gave butene fractions containing isomers.²⁶⁴ These fractions contained 16 and 30 per cent of butene-1, respectively; butene-2 was present but isobutene was absent. The recovered butene-2 contained 39 per cent of the *cis* and 61 per cent of the *trans* form. This isomerization of butene-2 at elevated temperatures is the reverse reaction of that observed in the case of butene-1. Hence, an equilibrium relationship exists between butene-1 and the *cis-trans* forms of butene-2. The mechanism of the formation of butene-1 probably involves dislocation of the double bond in *cis*-butene-2 (rather than the *trans* form). This statement is contingent upon there being a higher energy content in *cis* forms (over *trans*) at elevated temperatures. The equilibrium relationships would then assume the following order:



cis-Butene-2 (erroneously reported as *trans*) was partially isomerized into the *trans* form (6 per cent) and into butene-1 (6.6 per cent) in the presence of pure phosphoric acid at 100° and atmospheric pressure.²⁸⁵ Subsequently, the exothermic heats of hydrogenation of butene-1, *cis*-butene-2, and *trans*-butene-2 at 82° were found to be 30.341 ± 0.025 , 28.570 ± 0.019 , and 27.621 ± 0.021 kilocalories per gram-mole, respectively.^{304a} Subtraction of these heat quantities, that of *cis*-butene-2 being the minuend, gives -1.771 ± 0.031 and $+0.949 \pm 0.028$ kilocalories per gram-mole as the "heat of isomerization" of *cis*-butene-2 at 82° into butene-1 and into *trans*-butene-2, respectively. These values indicate the occurrence of (1) an endothermic or unfavorable isomerization of *cis*-butene-2 into butene-1, and (2) an exothermic, or much more probable, conversion of *cis*-butene-2 into the *trans* form.

n-Butenes are isomerized to isobutene at 294° in the presence of steam and a catalyst such as alumina, aluminum sulfate, Glukhov clay, "floridin," or phosphoric acid dried either on charcoal or "silicate" related to chamotte.^{199, 200} In this isomerization, polymers and gaseous alkanes were formed also. Likewise, a catalyst prepared by heating phosphoric acid with kieselguhr to 300° catalyzes the conversion of butene-1 and butene-2 into isobutene at about 325°. ^{420, 421} A related patent reports

a 33 per cent yield of isobutene.⁴¹⁷ Phosphoric acid on kieselguhr catalyzes the conversion of *n*-butenes into isobutene at temperatures from 325° down to 250°, but butene-1 at temperatures below 250° yields butene-2 instead of isobutene.^{609a}



A series of experiments⁵⁴⁰ is concerned with the equilibrium relationship between isobutene and a feed mixture of butene-1 (27 per cent), *cis*-butene-2 (29 per cent), and *trans*-butene-2 (44 per cent) at 265-426° in the presence of phosphoric acid dried on chamotte. It was found that the equilibrium concentration of isobutene at 300° is about equal to that of butene-1 plus butene-2, and that it decreases with rise in temperature in accordance with the following equation:^{199, 540}

$$\log_{10} K_p = \log_{10} \frac{\text{Isobutene}}{\text{Butene-1} + \text{Butene-2}} = \frac{304}{T} - 0.528$$

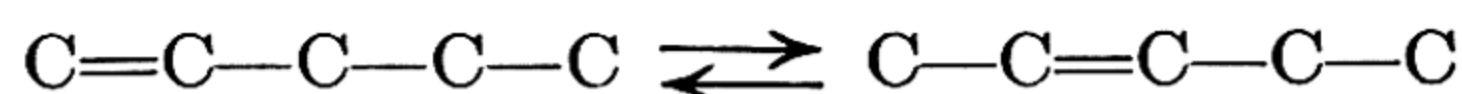
A comparison between the observed (304 multiplied by $R \log_e 10$) and calculated values of the heat of isomerization, Q , of *n*-butenes into isobutene is instructive:

Butene-1	$Q = 3.582$ kilocal./gram-mole (calc. for 25-82°)
<i>cis</i> -Butene-2	$Q = 1.811$ kilocal./gram-mole (calc. for 25-82°)
<i>trans</i> -Butene-2	$Q = 0.862$ kilocal./gram-mole (calc. for 25-82°)
<i>n</i> -Butenes (stated mixture)	$Q = 1.87$ kilocal./gram-mole (calc. for 25-82°)
<i>n</i> -Butenes (stated mixture)	$Q = 1.39$ kilocal./gram-mole (obs. at 265-426°)

The calculated and observed heats of isomerization for the mixture of *n*-butenes are not in good agreement, probably because of the 240-400° discrepancy in temperature imposed by limited calorimetric data on the individual isomers. The calculated exothermic heats of isomerization of butene-1, *cis*-butene-2, and *trans*-butene-2 into isobutene are practically identical with the accepted 25° values: 3.580, 1.810, and 0.860 kilocalories per gram-mole, respectively.^{581b, 586a} Other workers^{529a} assume that the ratio of isobutene to *n*-butenes is about 0.57 for equilibrium conditions at 400°. This value should be less than 0.50 if the parameters 304 and 0.528 of the foregoing equation^{199, 540} are correct.

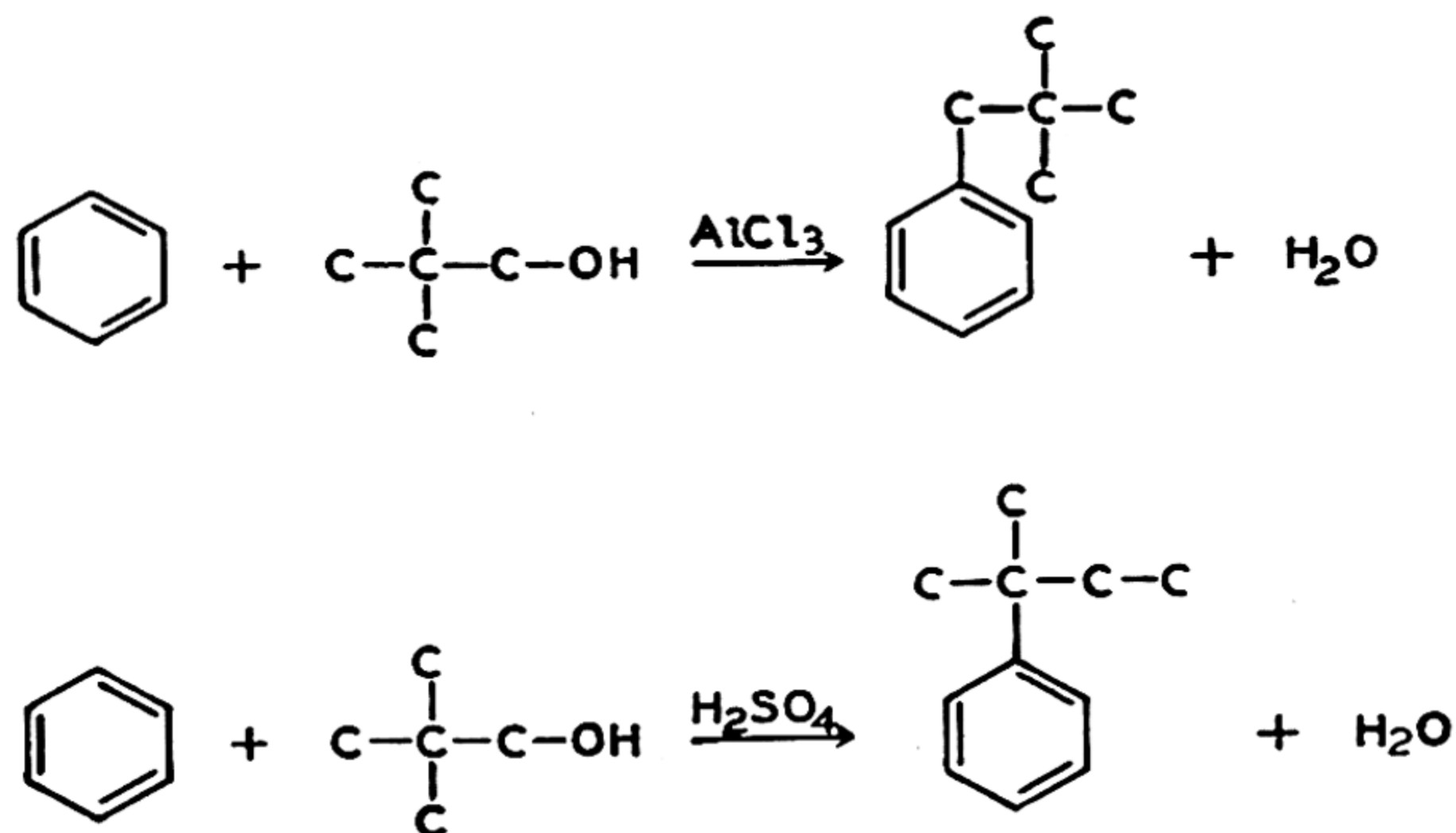
The isomerization of *n*-butenes into isobutene has been studied also in the presence of activated silica-aluminum at 385-600° with variable space velocities.¹⁵⁸ A 5.7-fold increase in space velocity at 600° changed the yield of isobutene only slightly (14.2 raised to 17.1 per cent), but decreased the side reactions so that the recovered *n*-butenes were 50.7 instead of approximately 36.8 per cent by weight of charged *n*-butenes.

Pentenenes. A partial interconversion of pentene-1 and pentene-2 at 550-600° apparently takes place without formation of branched-chain pentenes or of cyclopentane.^{261, 265} The last hydrocarbon has been considered a possible isomer.⁴⁹⁷



Pentene-1 yielded a mixture of 21.7 per cent of pentene-1 and 78.3 per cent of pentene-2 when repeatedly passed over activated alumina at 357°. ^{172a} Passage of pentene-1 at 400° over an activated silica-alumina catalyst gave 59 per cent by weight of 2-methylbutenes among other products.¹⁵⁸ A catalyst comprising silica, alumina, and thoria in the proportions 100:5:0.5 is recommended.^{581a} *n*-Pentenenes passed over calcined alumina at 450° form 2-methylbutenes.³³ Sodium permutite can be used for the same purpose at 400° and 450°. ^{257a}

Isomerization has been found to accompany the alkylation of benzene with pentene-1 in the presence of sulfuric acid at 5°. ²⁸⁷ The normal product, 2-phenylpentane, was obtained together with 3-phenylpentane, indicating an isomerization.* Isomerization in alkylation may interfere with synthesis of hydrocarbons.²⁸⁶ When such isomerization occurs, sulfuric acid leads to a more fundamental change in the structure than aluminum chloride.²⁸⁷ Neopentyl alcohol, for example, reacts with benzene to give neopentylbenzene in the presence of aluminum chloride, whereas sulfuric acid, as catalyst, gives *tert*-amylbenzene.⁴⁴² In the first case there is apparently a simple dehydration, but in the second reaction an isomerization occurs as well. Isomerization of hydrocarbons in an alkylation by alcohols apparently involves either the *rearrangement of an intermediary alkene prior to the alkylation*, or *isomerization of the primary dehydration product* formed by condensation between alcohol and hydrocarbon through direct loss of water.

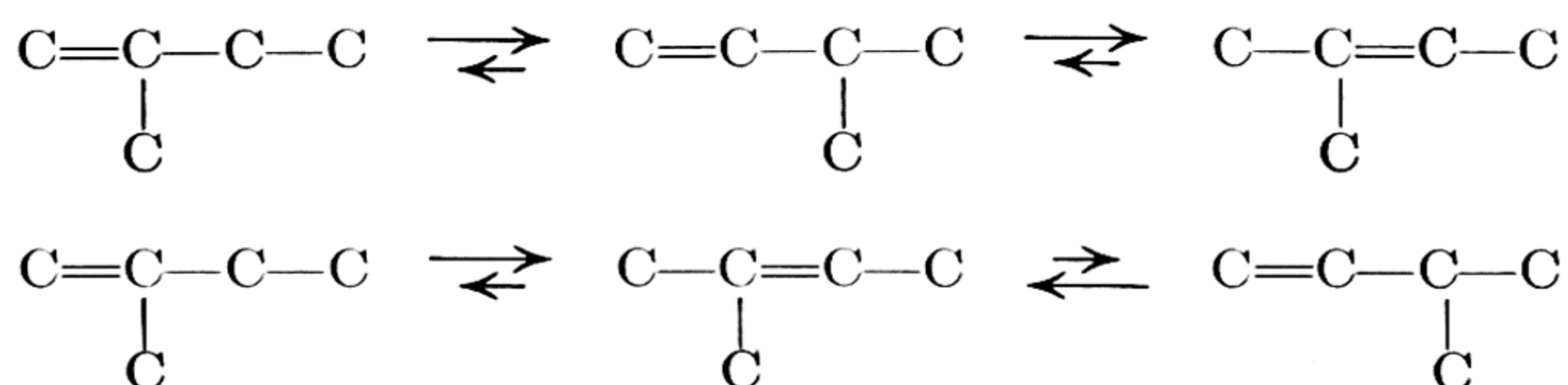


* The explanation of isomerization during alkylation in this and other examples remains incomplete to date. Further investigations of alkylation with various agents and of such competitive mechanisms as isomerizations of initial alcohols and of intermediate alkyl halides, esters, and alkenes are indispensable.

Pentene-2, heated at 600° in a carbonized silica tube, yielded decomposition products (carbon, methane, ethylene, propene, butene, butadiene-1-3, and hexene) but did not give branched-chain pentenes; only 33 per cent of pentene-2 was recovered.⁴¹³ The *cis* and *trans* forms of pentene-2 have been taken erroneously as electromeric forms^{98, 301, 302, 356, 357, 544, 545*} *Cis*-pentene-2 has been isomerized to *trans*-pentene-2 by heating at 90-100° in the presence of xylene,³⁰¹ by combined heating (70-80°) and long exposure to sunlight,⁵⁴⁵ and by exposure to ultraviolet light.⁵⁴⁵ It is quite possible that all three of these effects were purely thermal. However, solvents may have a small effect upon the isomerization. *Cis*-pentene apparently undergoes a slight transformation into the *trans* form when dissolved in acetic acid.⁹⁸ *Trans*-pentene-2 is converted partly into *cis*-pentene-2 upon exposure to ultraviolet light⁵⁴⁴ or upon dissolution in acetic acid.⁹⁸ Certain early experiments on the isomerization of pentene-2 are inconclusive.^{609aa}

Pentene-2 has been isomerized slightly to pentene-1 by prolonged catalysis over activated alumina at 266-364°, alumina plus cobaltous oxide at 320° and 375°, alumina plus chromic oxide at 295° and 345°, alumina plus ferric oxide at 295° and 344°, or alumina plus manganous oxide at 301-366°.^{172a} The yields of pentene-1 and pentene-2 at 364° averaged 15.3 and 84.7 per cent, respectively, which are probably the equilibrium values.

2-Methylbutene-1 was isomerized to an equilibrium mixture containing 27.0, 3.6, and 69.4 per cent of 2-methylbutene-1, 3-methylbutene-1, and 2-methylbutene-2, respectively, by a prolonged recirculation over activated alumina at 357°.^{172a} Products of practically the same composition as the foregoing mixture were obtained by similar treatments of 3-methylbutene-1 at 362° and of 2-methylbutene-2 at 356°. *n*-Pentenes were absent in these isomerizates. Reaction rate studies would enable a decision to be made concerning the following theoretical mechanisms for the foregoing isomerizations:



Probable values of the equilibrium mixture compositions and corresponding equilibrium constants for branched pentenes, calculated from

* Physical constants of *cis*- and *trans*-pentene-2¹⁵⁴ have been found of considerable value in distinguishing the recorded "electromeric," "isomeric," "lower-boiling," "higher-boiling," "labile," and "stable" forms.

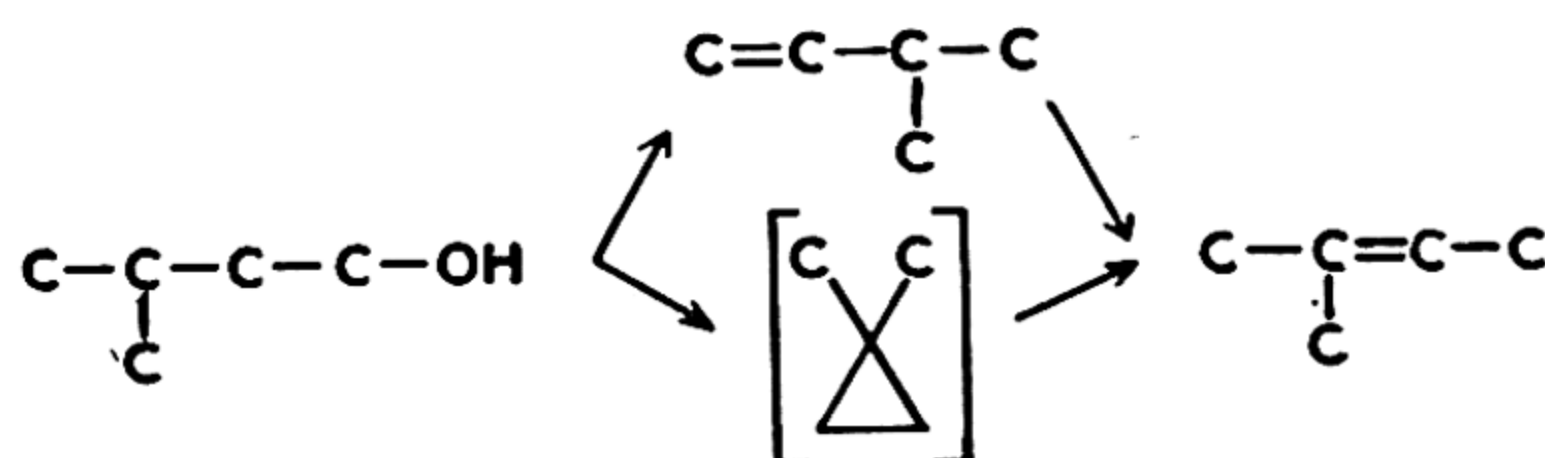
data ^{172a} mainly on isomerization of 2-methylbutene-2, are given in the following compilation:

Temp. (°C.)	Equilibrium Concentrations, weight per cent			Probable Equilibrium Constants		
	$\text{C}=\text{C}-\text{C}-\text{C}$ C	$\text{C}=\text{C}-\text{C}-\text{C}$ C	$\text{C}-\text{C}=\text{C}-\text{C}$ C	$K_1 = \frac{\text{C}-\text{C}=\text{C}-\text{C}}{\text{C}=\text{C}-\text{C}-\text{C}}$ C	$K_2 = \frac{\text{C}-\text{C}=\text{C}-\text{C}}{\text{C}=\text{C}-\text{C}-\text{C}}$ C	$K_3 = \frac{\text{C}=\text{C}-\text{C}-\text{C}}{\text{C}=\text{C}-\text{C}-\text{C}}$ C
251	22.6	1.8	75.6	3.35	42.0	12.6
300	25.6	2.5	71.9	2.81	28.8	10.2
358	27.3	3.5	69.2	2.53	19.8	7.8
400	28.2	5.0	66.8	2.37	13.4	5.6

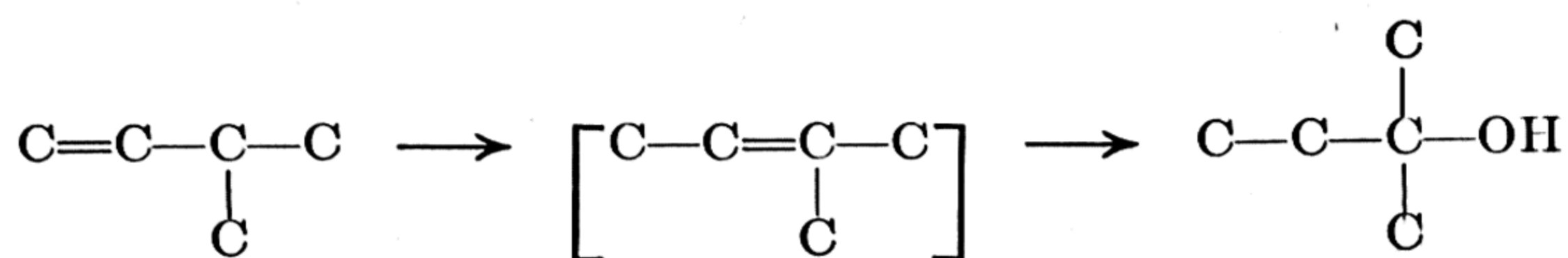
These data indicate that the concentration of 3-methylbutene-1 is doubled by a 100° increase in temperature. The heats of hydrogenation of 2-methylbutene-1, 3-methylbutene-1, and 2-methylbutene-2 at 82° are 28.491 ± 0.10 , 30.336 ± 0.06 , and 26.920 ± 0.06 kilocalories per gram-mole of vapor, respectively.^{140a, 305} Appropriate subtraction of these heat quantities gives 1.571 ± 0.12 , 3.416 ± 0.08 , and 1.845 ± 0.12 kilocalories per gram-mole of vapor at 82° as the exothermic heats of isomerization corresponding to equilibria K_1 , K_2 , and K_3 .

Isomerization of 3-methylbutene-1 into 2-methylbutene-2 (55-80 per cent) in the presence of alumina at 450-560° was reported to occur irreversibly.²⁷¹ Alumina at 450°, aluminum sulfate at 425°, and phosphoric acid on pumice at 500°, as catalysts in the isomerization of 3-methylbutene-1, gave 10, 47, and 29 per cent yields of 2-methylbutene-2, respectively.⁴¹³ These isomerizations also were found to be irreversible.

In isomerization of 3-methylbutene-1 to 2-methylbutene-2 by heating the pure hydrocarbon or during the dehydration of isoamyl alcohol, the relative effectiveness of alumina and aluminum sulfate as catalysts is always the same. The conversion into 2-methylbutene-2 is greater when the alcohol is dehydrated. Isoamyl alcohol and alumina at 450° gave an "amylene" containing 90 per cent of 3-methylbutene-1, but isoamyl alcohol and aluminum sulfate at 345° formed an "amylene" having about 79 per cent of 2-methylbutene-2.⁴¹³ In the dehydration giving 2-methylbutene-2, 1,1-dimethylcyclopropane may be an intermediate product:

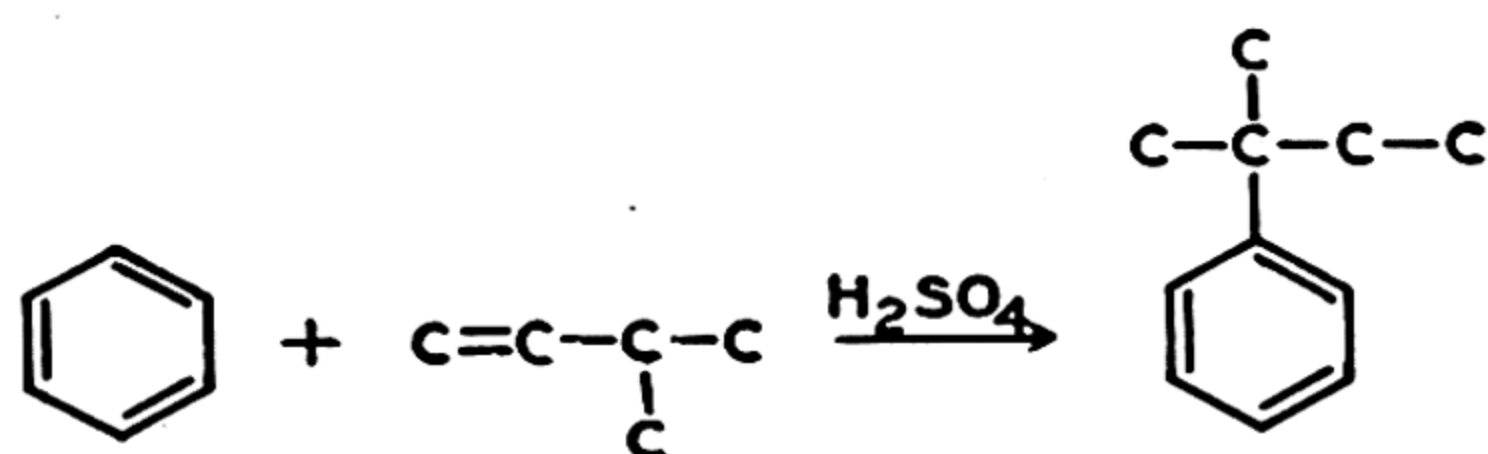


The action of 60-per cent sulfuric acid on 3-methylbutene-1 for one hour at 38° gave a polymer and a solution from which *tert*-amyl alcohol was recovered.⁴¹³ The formation of *tert*-amyl alcohol may involve an intermediary isomerization of 3-methylbutene-1 into 2-methylbutene-2:

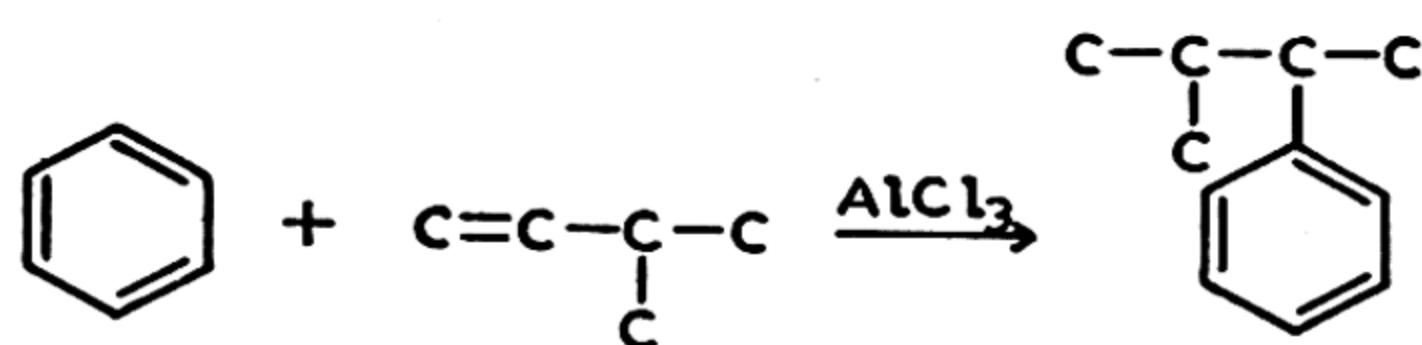


At the slightly lower temperature of 30-35°, 3-methylbutene-1 is stable toward 60-per cent sulfuric acid. An isomerization into 2-methylbutene-2 can take place, though only to a slight extent, by the use of an acid of such concentration that polymerization does not occur appreciably.⁴¹³

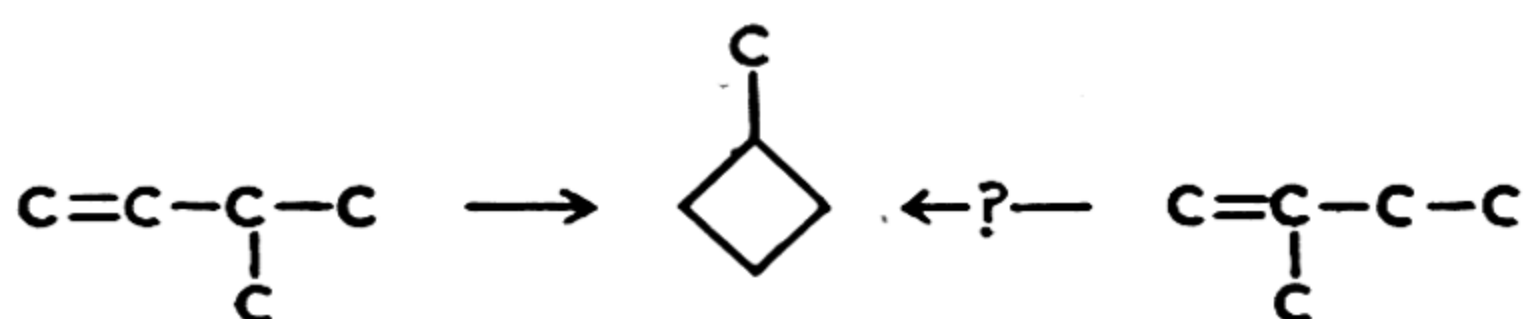
The isomerization of 3-methylbutene-1 into 2-methylbutene-2 may occur also in the alkylation of benzene to *tert*-amylbenzene by 3-methylbutene-1 in the presence of 96-per cent sulfuric acid at 0°:²⁸⁶



However, aluminum chloride at 4-6° leads to the normal product, 2-methyl-3-phenylbutane:²⁸⁷



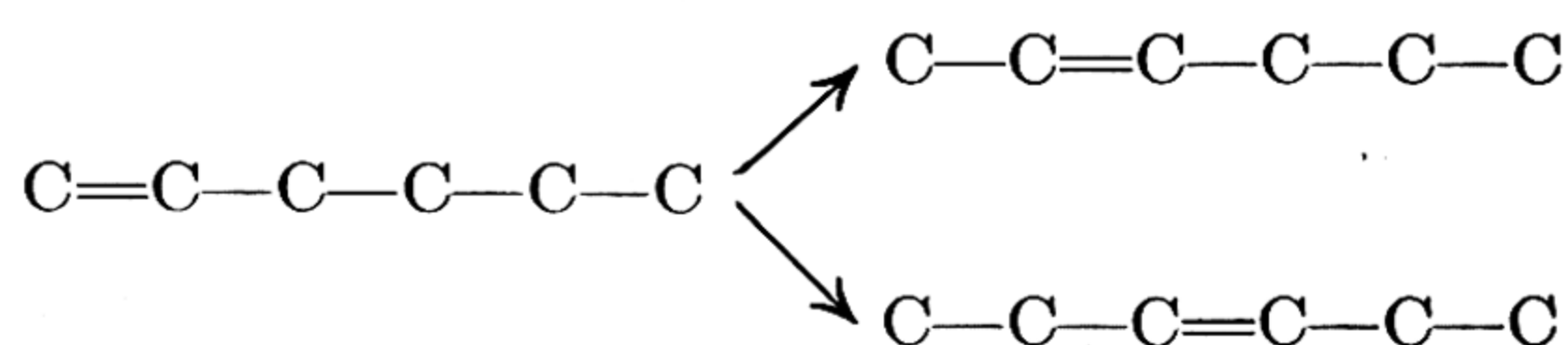
Amylene boiling up to 42° C. (impure!), prepared according to Würtz⁶⁵⁷ and Eltekov,¹⁶³ was isomerized by treatment with 50 per cent of aluminum chloride for 5 weeks at 0-20°.¹⁶ The reaction was given as a cyclization of 3-methylbutene-1 into methylcyclobutane and formation of heavier cyclanes and alkanes. A cyclization of 2-methylbutene-1, which is a possible component of the amylene, could have occurred, but has never been considered or verified:



A small amount of work has been conducted on the equilibrium between 2-methylbutene-2 and *n*-pentenes at 400° in the presence of a permutite catalyst.^{529a} The equilibrium product has 80 per cent of 2-methylbutenes, after correcting for side products amounting to 15 per cent.

Hexenes. Hexene-1, heated one hour at 400° under 40(?) atmospheres' initial pressure of hydrogen in the presence of 5 per cent of molybdenum trisulfide, formed a significant amount of hexene-2 and some

hexene-3, indicating that isomerization occurs by a shifting of the double bond.⁴³⁷ Hexenes of iso-structure were not isolated, neither was there any change in hexene-1 heated with molybdenum trisulfide for one hour at 300°. Hardly any side products boiling lower than hexene-1 were formed at 400°, in contrast with heptane and octane treated under the same conditions, but polymerization began at 350° and was considerable at 400°.



Thermodynamic data^{497, 651} predict that hexene-1 should form cyclohexane and methylcyclopentane, but these products have not been reported.

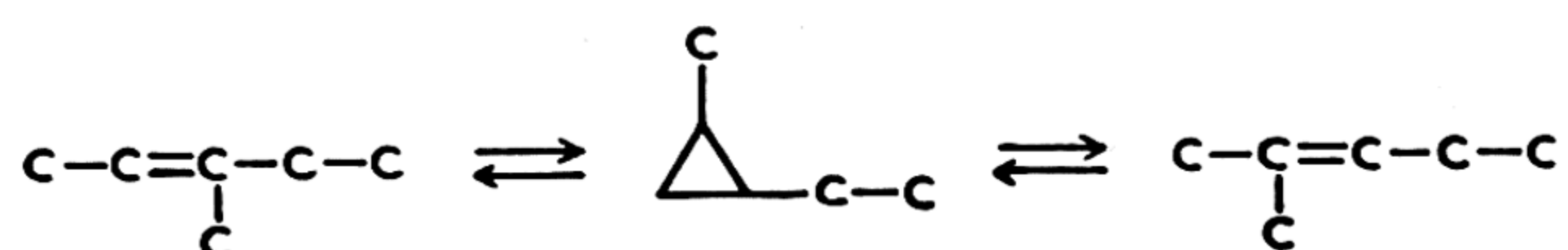
n-Hexenes form 3-methylpentene-2 and/or 2-ethylbutene-1 when passed over alumina at 400°, according to an old patent.³³ Recently, hexene-1 was passed over alumina at 398° at varying rates, as well as over thoria.²²⁰ The products* included isomers, such as hexene-2, hexene-3, 2-methylpentene-2, 3-methylpentene-2, and 2-ethylbutene-1, some of which were again passed over the catalysts under comparable conditions; the results are presented in Table 8. These investigators formulated the following conclusions on isomerization of hexenes:

Table 8. Isomerization of Hexenes as Related to Their Structure, Reaction Conditions and Products²²⁰

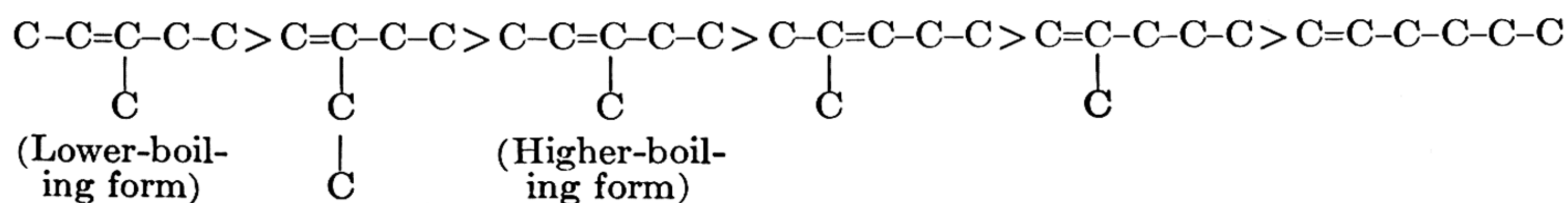
Reactants		Conditions		Percentage Composition of Products									
Hexene	Catalyst	cc. Hexene feed per hour per 10 g. catalyst	Temp. (°C.)	Hexene-1	Hexene-2	Hexene-3	2-Methyl-pentene-1	2-Methyl-pentene-2	Lower-boiling 3-Methyl-pentene-2	Higher-boiling 3-Methyl-pentene-2	2-Ethyl-butene-1	Isohexane	Polymers
Hexene-1	Al ₂ O ₃	3.1	398	5.9	..	11.3	..	27.7	9.8	5.3	38.7	..	.
Hexene-1	Al ₂ O ₃	11.2	398	24	2	8	..	12	36	5	13	..	.
Hexene-1	Al ₂ O ₃	22.5	398	89	9.2	..	1.8	..	.
Hexene-1	Al ₂ O ₃	45.5	398	92	8
Hexene-1	ThO ₂	3.12	398	90	..	5	..	5
2-Methylpentene-2	Al ₂ O ₃	3.12	398	62	35	3
2-Methylpentene-2	ThO ₂	3.12	398	2	70	..	25	..	3
Lower-boiling 3-methylpentene-2	Al ₂ O ₃	3.12	398	22	70	..	5	..	3
Lower-boiling 3-methylpentene-2	Al ₂ O ₃	3.12	440	29	8	52	..	6	2	3
Lower-boiling 3-methylpentene-2	ThO ₂	3.12	398	7	70	..	19	..	4
Lower-boiling 3-methylpentene-2	ThO ₂	3.12	440	16	5	40	..	30	3	6
2-Ethylbutene-1	ThO ₂	3.12	398	2	69	..	26	..	3

* Recent work^{473, 642} on the separation of isomeric hexenes by fractional distillation sharply contradicts the reported "facile" separation of these isomerization products.

1. The straight-chain hexene is the least stable at 400°.
2. The 2-methylpentenes give the corresponding 3-methylpentenes in large quantities.
3. The 2-ethylbutene-1 is the result of double-bond migration.
4. 2-Ethylbutene-1 passed over thoria gives the same product as that obtained from the 2- and 3-methylpentenes.
5. Increase in temperature to 440° causes the shift of the double bond to the end of the chain and the formation of 2-methylpentene-1. Isohexane is formed simultaneously as a result of dehydrogenation-hydrogenation.
6. The products are in agreement with the hypothesis of an activated-intermediate stage, actually a cyclization of hexenes into unstable substituted cyclopropanes, *e.g.*,



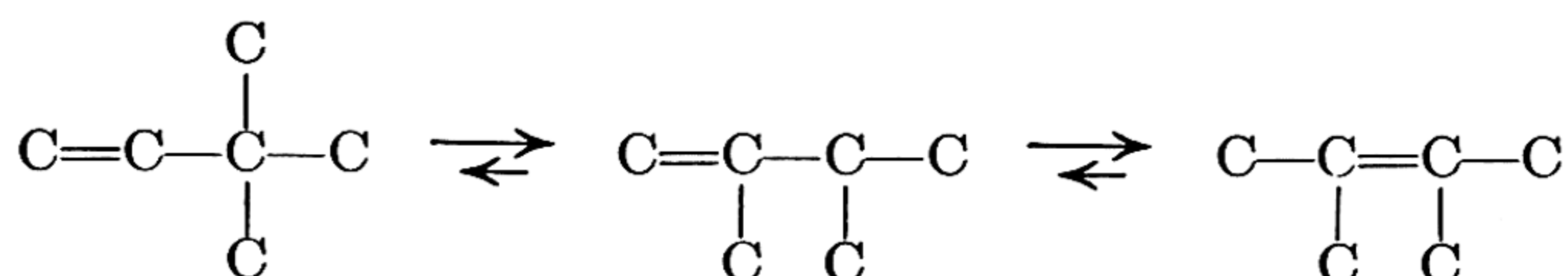
7. The order of stability at 400° was found to be as follows:



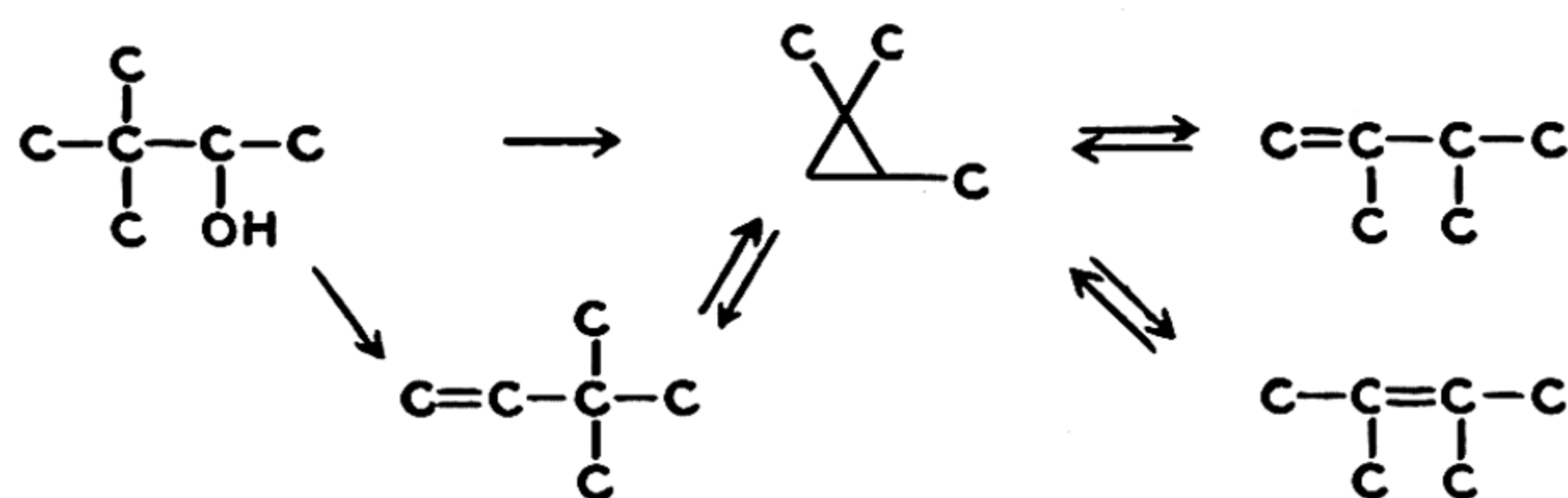
The catalytic action of zinc chloride on pumice (1:1) upon hexene-1 was studied for the purpose of finding out whether an isomerization would occur with the change of carbon-chain configuration.⁴³⁶ The amount of isomers (23 per cent) was determined by hydrogenating the product and then determining the tertiary carbon-atom content by the antimony pentachloride method. The reaction took place in 1.5 hours at 300-325° and 50 atmospheres' initial pressure of nitrogen, with formation of over 15 per cent of high-boiling side products. Hexene-1, heated 4-5 hours at 325-350° with phosphoric acid on pumice (1:1) under 60 atmospheres' pressure, gave approximately 15 per cent of 2-methylpentene-2.⁴³⁸

Treatment of 3,3-dimethylbutene (*tert*-butylethylene) with phosphorus pentoxide on silica gel at 300° gave 15 per cent of 2,3-dimethylbutene-1, 30 per cent of 2,3-dimethylbutene-2, together with traces of 3,3-dimethylbutene and a considerable amount of a polymerized product.³²⁹ A similar contact with sodium permutite at 310° showed almost complete conversion into 2,3-dimethylbutenes-1 and -2.^{267a, 529a} Activated alumina at 350° is without action on 3,3-dimethylbutene, but anhydrous aluminum sulfate at 275° gives 29.7 per cent of 2,3-dimethylbutene-1,

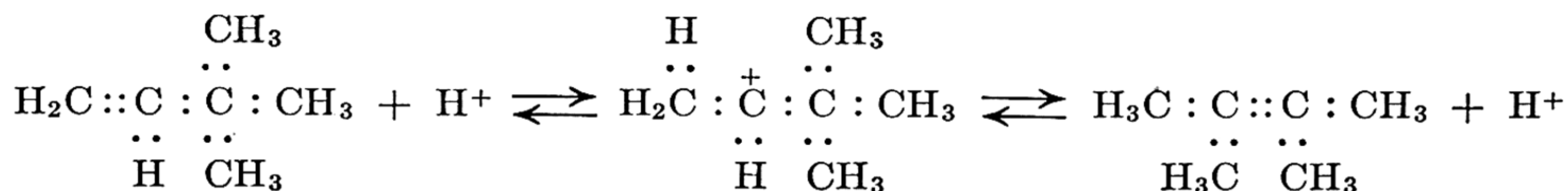
55.5 per cent of 2,3-dimethylbutene-2, together with 3.8 per cent of 3,3-dimethylbutene.¹³⁰ Individual treatments³²⁹ of 2,3-dimethylbutene-1 and 2,3-dimethylbutene-2 with phosphorus pentoxide on silica gel at 300° gave quantitatively the same products as did 3,3-dimethylbutene. In a previous investigation,⁶⁴³ the dehydration of pinacolyl alcohol over phosphorus pentoxide on silica gel at 300° gave isomeric hexenes in the proportions: 3,3-dimethylbutene (3 parts), 2,3-dimethylbutene-1 (31 parts), and 2,3-dimethylbutene-2 (61 parts). From these facts, it was concluded that an equilibrium state exists among these hexenes. This equilibrium, including reaction displacements, can be formulated as follows:



As an alternative explanation to the foregoing equilibria, the dehydration of pinacolyl alcohol and the interconversions of 3,3-dimethylbutene, 2,3-dimethylbutene-1, and 2,3-dimethylbutene-2 may be considered as due to an intermediary formation of 1,1,2-trimethylcyclopropane:



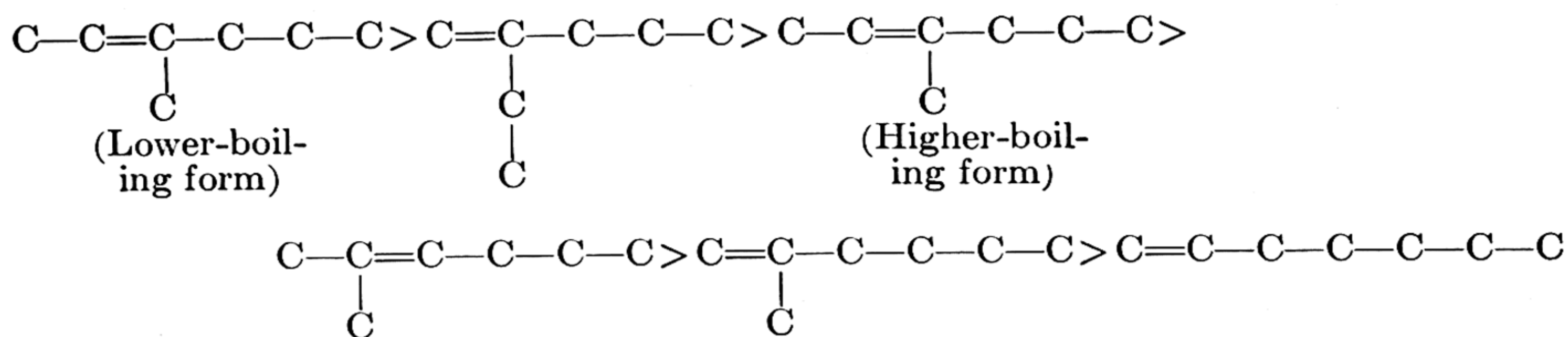
An older mechanism proposed for the interconversion of these hexenes is the addition of a proton from the catalyst to one of the carbon atoms of a double bond, leaving the other carbon atom temporarily with only six electrons:³²⁹



This general mechanism is objected to by several investigators^{38, 93, 425} because it involves positive carbonium ions. A modern and more "complete" mechanism should consider resonance energy and solvent effects, partial valences, and activated-complex formation.⁶³⁵

Heptenes. The isomerization of heptenes has been studied mainly by two investigators.²²⁰ Heptene-1, passed over alumina at 398°, gave 70 per cent of 3-methylhexene-2 and 5 per cent of 2-ethylpentene-1. Pas-

sage of 2-methylhexene-2 at 398° over alumina or thoria resulted respectively in 40 and 72 per cent of 3-methylhexene-2, along with 15 and 20 per cent of 2-ethylpentene-1. The treatment of 3-methylhexene-2 at 398° with thoria or alumina gave respectively 2 and 10 per cent of 2-methylhexene-2, together with 15 and 2 per cent of 2-ethylpentene-1. Increase of temperature to 440° in the last two cases resulted in the formation of 11 and 18 per cent of 2-methylhexene-1, and 7 and 4 per cent of isohexane. Passage of 2-ethylpentene-1 over thoria at 398° yielded 3 per cent of 2-methylhexene-2 and 71 per cent of 3-methylhexene-2. The isomerizations of these heptenes are compared in Table 9. The conclusions to be gathered from this table are analogous to those given for isomerization of hexenes under identical conditions. The following order of stability of heptenes at 400° was given:



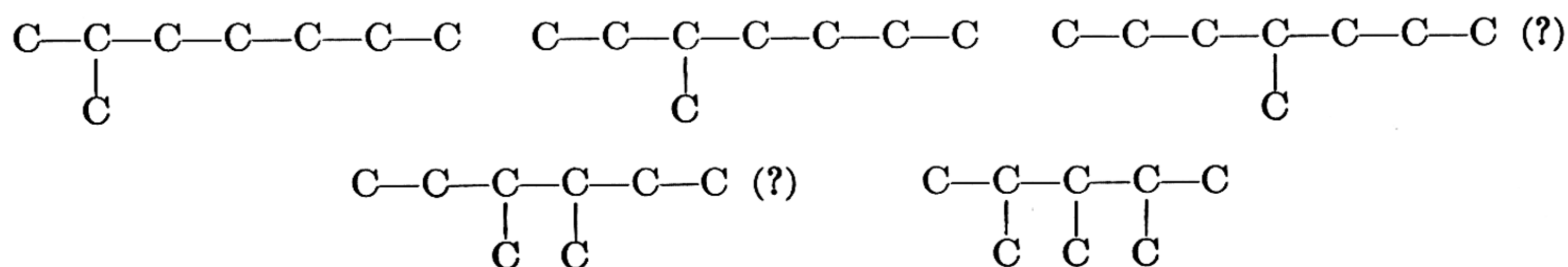
Heptene-1 (b.p. 91.9-92.0°/741 mm. Hg, $D_4^{20}=0.6974$, $n_D^{20}=1.4000$) probably formed a small amount of 3-methylhexene-2 when passed slowly over beryllium oxide at 450°. ^{12a} The main fraction (b.p. 92-95°, n_D^{20}

Table 9. Isomerization of Heptenes as Related to their Structure, Reaction Conditions and Products.²²⁰

Reactants		Conditions		Percentage Composition of Products						
Heptene	Catalyst	cc. Heptene fed per hour per 10 g. catalyst	Temp. (°C.)	Heptene-1	2-Methyl- hexene-1	2-Methyl- hexene-2	3-Methyl- hexene-2	2-Ethyl- pentene-1	Isohexane	Polymers
Heptene-1	Al ₂ O ₃	3.12	398	25	70	5
2-Methylhexene-2	Al ₂ O ₃	3.12	398	42	40	15	..	5
2-Methylhexene-2	ThO ₂	3.12	398	3	72	20	..	5
3-Methylhexene-2	Al ₂ O ₃	3.12	398	10	82	2	..	6
3-Methylhexene-2	Al ₂ O ₃	3.12	440	..	18	5	63	3	4	7
3-Methylhexene-2	ThO ₂	3.12	398	2	76	15	..	7
3-Methylhexene-2	ThO ₂	3.12	440	..	11	8	45	20	7	9
2-Ethylpentene-1	ThO ₂	3.12	398	3	71	21	..	5

=1.4074) of the once-through product was re-treated to form a richer condensate (b.p. 92-96°, $D_4^{20}=0.7041$, $n_D^{20}=1.4082$). The latter was hydrogenated at 140° in the presence of platinized charcoal, yielding a *n*-heptane and 3-methylhexane mixture (b.p. 92.0-96.0°/749 mm. Hg, $D_4^{20}=0.6836$, $n_D^{20}=1.3889$).

Octenes. Heating a mixture of octene-1 and octene-2 at 295-365° in quartz tubes gave a low-boiling product, corresponding to one per cent of isoöctenes and "practically" no gases.²⁵⁹ Zinc chloride, zinc chloride on pumice (1:1), and phosphoric acid on pumice (1:1) catalyzed the isomerization of an octene-1 and octene-2 mixture to "iso-products" accompanied by low- and high-boiling side products.⁴³⁶ These processes all required large amounts of "catalyst"; they gave a higher degree of isomerization in a shorter time when under nitrogen pressure. The mixed octene-1 and octene-2 heated in the presence of zinc chloride at 325-350° for 25 hours under atmospheric pressure, or for 1.5 hours at 300-325° under 50 atmospheres' initial pressure of nitrogen, yielded respectively 12 and 46.8 per cent of iso-compounds upon hydrogenation.⁴³⁶ An activated silica-alumina mass converted a mixture of octene-1 and octene-2 (prepared by the dehydration of octanol-2) into 58.2 and 60.5 per cent by weight of branched-chain octenes at 375° and 385°, respectively, prior to active cracking.¹⁵⁸ The products (branched-chain octenes) were next hydrogenated in the presence of a nickel catalyst, giving the following alkanes:

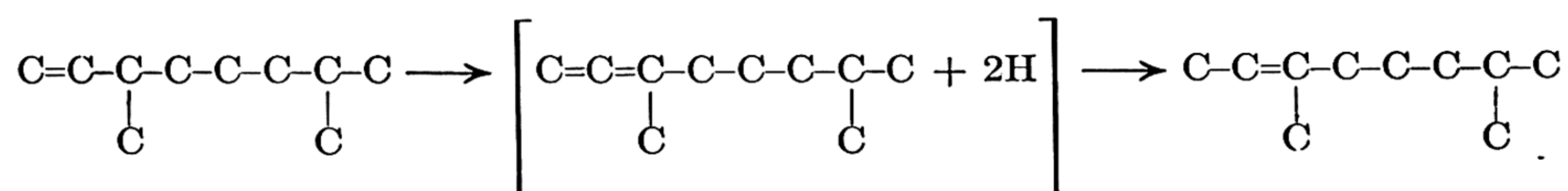


Hence, the isomerization of the mixture of octene-1 and octene-2 gave the following isomers*: 2-methylheptene-*x*, 3-methylheptene-*x* and/or 2-ethylhexene-1; 4-methylheptene-*x* and/or 2-propylpentene-1; 3,4-dimethylhexene-*x* and/or 2-ethyl-3-methylpentene-1; 2,3,4-trimethylpentene-*x* and/or 2-isopropyl-3-methylbutene-1. It was stated that following the initial isomerization there occurs a catalytic decomposition into propene, butenes, and pentenes. Therefore, it appears that the primary reaction is chiefly isomerization, and that decomposition essentially follows the isomerization. Both primary and secondary reactions apparently involve C—C ruptures, but differ in their extent and mode of recombination. The conclusion "cracking for the most part followed isomerization" of octenes¹⁵⁸ is based upon the presence of about equal proportions of *n*-butenes as compared to isobutene in gases accompanying the reaction, and upon an observed much slower isomerization of *n*-butenes into isobutene over the catalyst at a corresponding rate of flow. Other experimenters³⁹⁷ claim that thermal treatment of octene-1 and octene-2 at 345-380° leads to polymers and that increased

* Tentatively, since the locations of double bonds are still unknown.

thermal effect and reaction duration gives isoöctenes due to depolymerization. The last experiments are difficult to interpret, because of an 8.3 per cent content of isoöctenes in the material charged, as determined by the antimony pentachloride method. A catalyst comprising silica, alumina, and thoria in the proportions 100:5:0.5 is recommended for the isomerization of *n*-octenes into branched octenes.^{581a} Sodium permittite has also been used for this purpose.^{257a, 417a, 421a} Phosphoric acid can effect a conversion of 2,4,4-trimethylpentenes-1 and -2 into a 2,3,4-trimethylpentene, but the details of these isomerizations are lacking.^{561a}

Decenes. An exceptionally complete isomerization of 3,7-dimethyloctene-1 into 3,7-dimethyloctene-2, by double-bond shifting, occurred upon passage over a palladium-asbestos catalyst at 200° in a stream of carbon dioxide.⁶⁷⁰ Formation of an allene intermediate was proposed:



Hexadecene. Passage of cetene over an activated silica-alumina catalyst at 300°, 350°, 400°, and 450° gave 8.0, 44.9, 26.9, and 13.0 per cent by weight, respectively, of lower-boiling hexadecenes, assumed to have branched-chain structure.¹⁵⁸ It was postulated that following the initial isomerization, a decomposition to numerous smaller hydrocarbons occurs.

The experimental data on the isomerization of alkenes in the presence of various catalysts are presented in Table 10, p. 244.

Conclusions

1. An isomerization of alkenes unaccompanied by the formation of side products, proceeds by an apparent shifting of the hydrogen atom, resulting in change of double-bond position or in *cis-trans* isomerization.

2. A more extensive transformation with change in carbon-chain configuration takes place under more severe conditions (higher temperature, stronger catalyst). This involves two consecutive reactions: loosening of the C—C bond in the presence of the catalyst (dealkylation or "depolymerization") and recombination (such as alkylation by radicals and alkenes; or polymerization). Under these conditions cyclization can occur also.

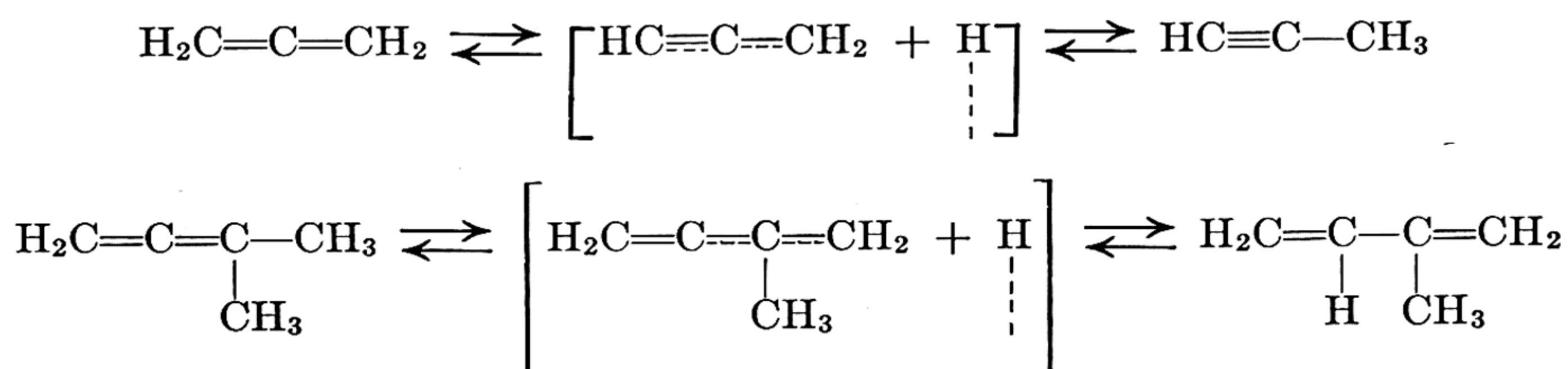
3. Side products, *i.e.*, smaller and larger molecules, accompany an isomerization with chain branching, because of the ease with which the branched alkenes can be polymerized and depolymerized.

ALKADIENES

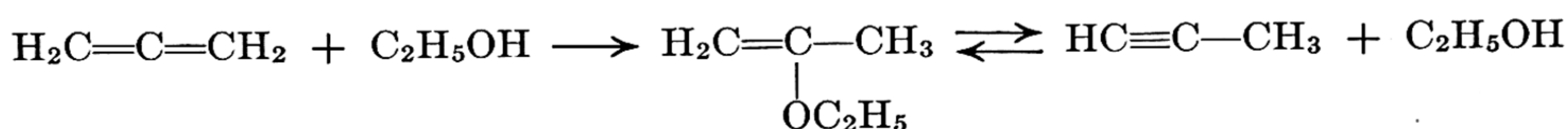
The unsaturated aliphatic hydrocarbons containing two double bonds are highly reactive. They readily undergo hydrogen-atom migration by shifting of double bonds, cyclization, or polymerization. Because of differences in structure and mechanism, the members of this group are considered separately as allenic and non-allenic alkadienes.

Allenic Alkadienes

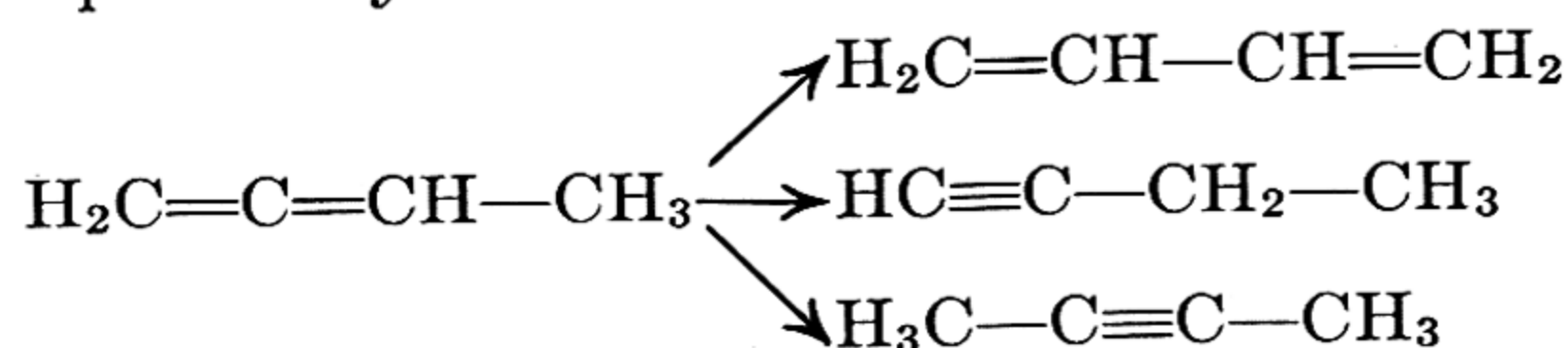
The thermal isomerizations of alkadienes apparently involve "detachment" of hydrogen:



Propadiene (*i.e.*, allene), when passed over "Floridin" at 167-350°, yielded propyne (*i.e.*, allylene) and polymers.⁵⁵² Heated with ether and sodium at 100°, propadiene yielded the sodium derivative of propyne.²³⁹ Propadiene, treated 12 hours at 160-170° with alcoholic potash,* gave propyne and ethyl isopropenyl ether (intermediate product), together with *unreacted propadiene*.¹⁷⁹ The mechanism of isomerization and the presence of propadiene in the product will be considered again under the Alkynes:

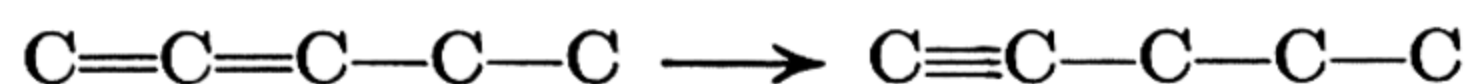


Butadiene-1,2 (*i.e.*, methylallene), in the presence of "Floridin" at 245-300°, isomerized to 3.4 per cent of butyne-1 and traces of butadiene-1,3.⁵⁴⁹ Butadiene-1,2 heated with sodium and ether, or with alcoholic potash, gave a butene plus the sodium derivative of butyne-1, and free butyne-2, respectively.²⁹²

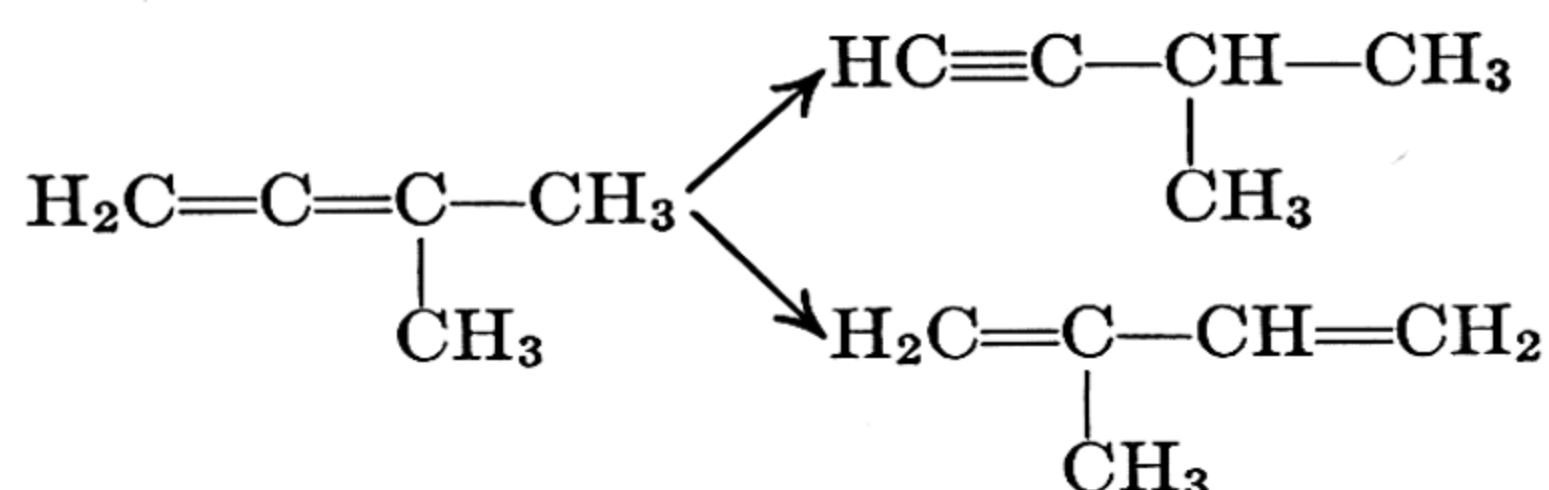


* "Alcoholic potash" results when potassium hydroxide and anhydrous ethanol are mixed, forming potassium ethoxide and water. This reaction is reversible and is favored by heating of the mixture, but then some secondary reactions occur.⁶⁴⁹ The resultant or even accidentally introduced water influences the isomerization to an unknown extent, so that it seems desirable to repeat some of the experiments in the presence of pure potassium ethoxide (devoid of ethanol and water).

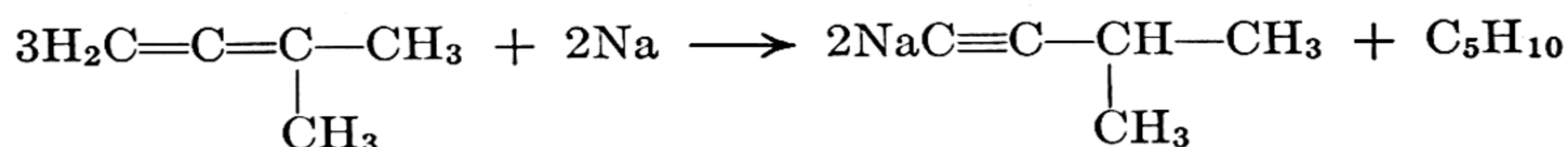
Pentadiene-1,2 (ethylallene) with xylene or petroleum of boiling point above 180° , treated 2 hours at 140° with a slight excess of sodamide (suspended in Vaseline), gave the sodium derivative of pentyne-1.⁷⁹ As the reaction mixture approached $100-120^{\circ}$, ammonia gas was liberated.



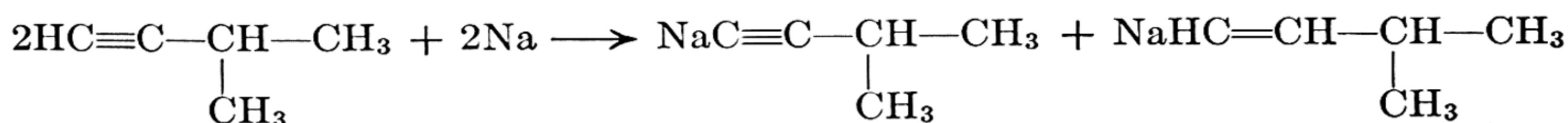
3-Methylbutadiene-1,2 (unsym-dimethylallene), at $215-334^{\circ}$ in the presence of activated "Floridin," isomerized incompletely into 2-methylbutadiene-1,3 (isoprene) and 3-methylbutyne-1 (isopropylacetylene).⁵⁴⁸ 3-Methylbutadiene-1,2, heated alone at $100-225^{\circ}$ in sealed tubes, gave several types of polymers and a small amount of 2-methylbutadiene-1,3.³³⁰ Alumina at 300° catalyzed an isomerization of 3-methylbutadiene-1,2 into 2-methylbutadiene-1,3.^{31, 638}



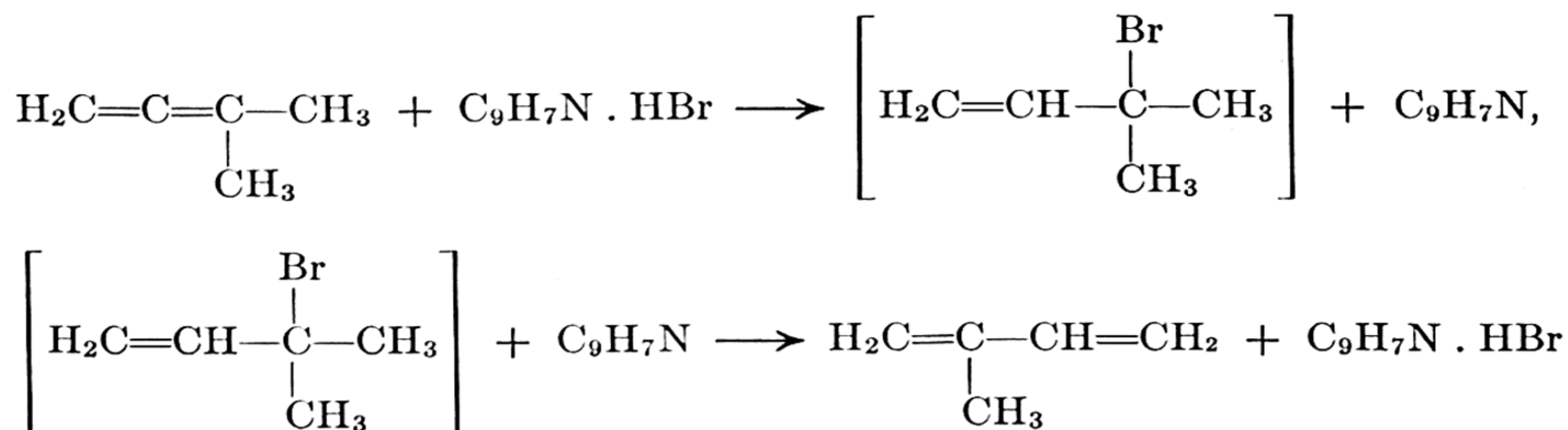
3-Methylbutadiene-1,2, heated with sodium at 100° , gave the sodium derivative of 3-methylbutyne-1, hydrolyzed by water to the alkyne.¹⁷⁶ The reaction was presumed to follow the equation,¹⁷⁷

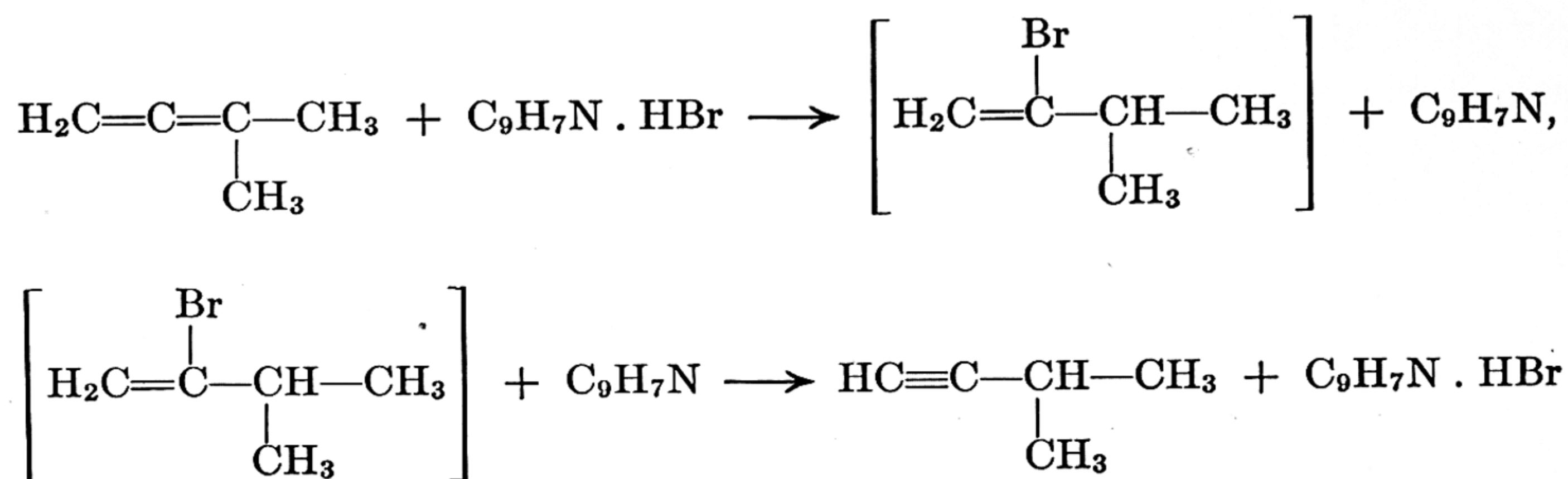


which is in disagreement with a previous explanation:¹⁶⁴

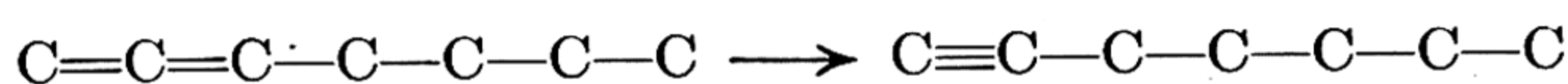


Heating of 3-methylbutadiene-1,2 with quinoline hydrobromide resulted in the irreversible formation of 50-55 per cent of 2-methylbutadiene-1,3, together with some 3-methylbutyne-1.³²⁶ The reaction mechanism proposed was as follows:

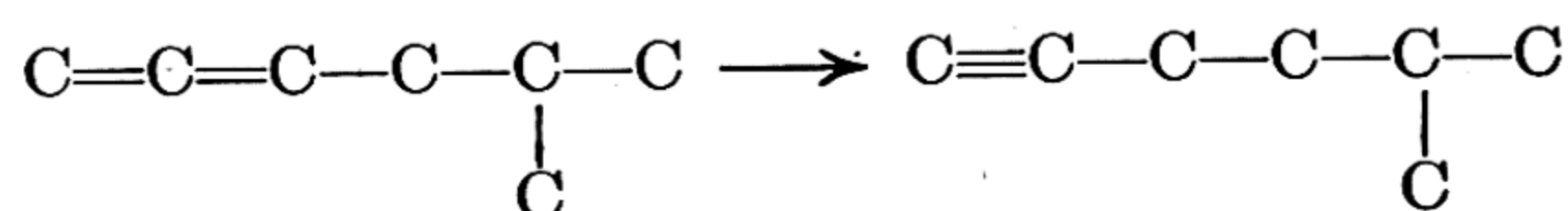




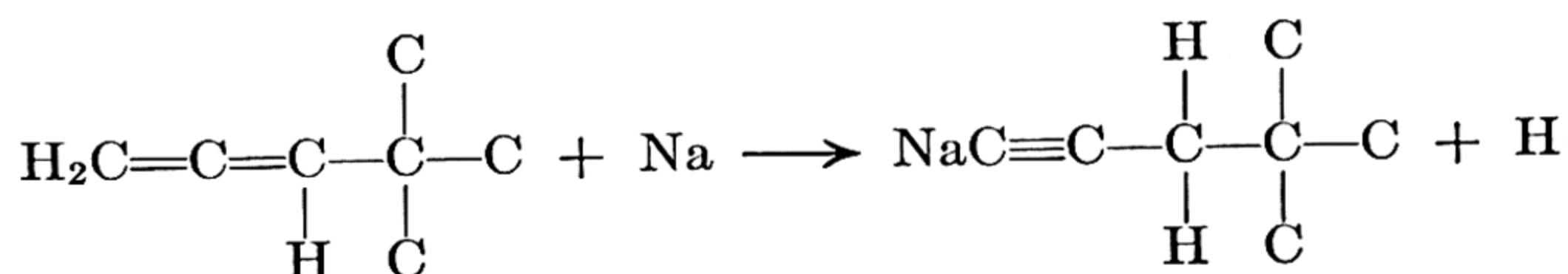
Heptadiene-1,2 (*n*-butylallene) with xylene or petroleum of boiling point above 180°, treated for 2 hours at 140° with a slight excess of sodamide (suspended in Vaseline), gave the sodium derivative of heptyne-1 and liberated free ammonia.⁷⁹



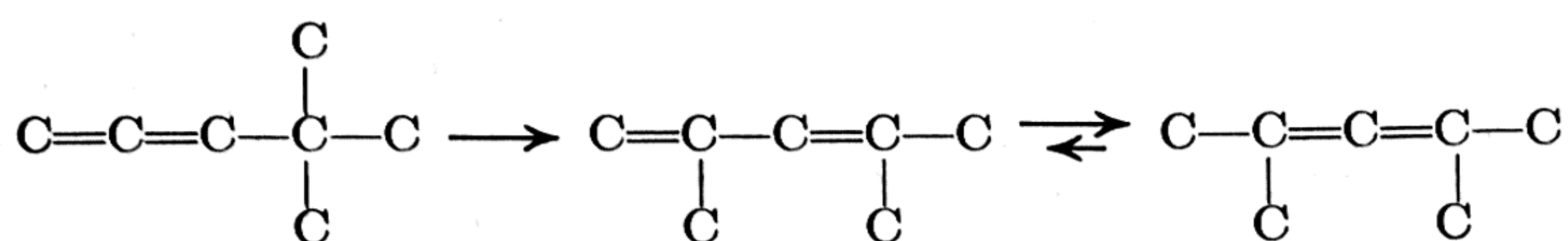
5-Methylhexadiene-1,2 (isobutylallene) gave the sodium derivative of 5-methylhexyne-1 in good yield⁷⁹ when treated with sodamide as in the foregoing experiment. Free ammonia was liberated at 100-120°.



4,4-Dimethylpentadiene-1,2 (*tert*-butylallene), heated with sodium, formed the sodium derivative of 4,4-dimethylpentyne-1.¹⁸² This reaction involves the removal of 2 terminal hydrogens, one of these by a 3-carbon type of hydrogen migration and the other by displacement with sodium:

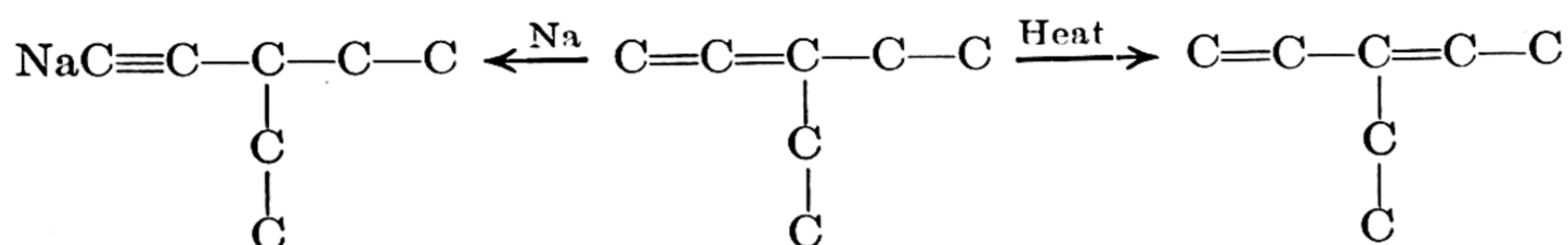


4,4-Dimethylpentadiene-1,2 (*tert*-butylallene), when passed over "Floridin" at 230-235°, gave successively 2,4-dimethylpentadiene-1,3 and 2,4-dimethylpentadiene-2,3 (tetramethylallene).⁵⁵³ The equilibrium relationships, disregarding polymerization, favor complete transformation of 2,4-dimethylpentadiene-1,3 into 2,4-dimethylpentadiene-2,3, as demonstrated by a study of mixtures at 120-206° in the presence of "Floridin."⁵⁵¹ The initial formation of 2,4-dimethylpentadiene-1,3 merits further study; it may be considered as a rare instance of the shift of an alkyl and an unsaturated bond, *without* hydrogen transfer. This isomerization is patterned after the ordinary allylic rearrangement, and is part of the following "right-shift" of equilibrium:



2,4-Dimethylpentadiene-2,3, heated for 5 days at 150°, was largely polymerized, but part of it isomerized into 2,4-dimethylpentadiene-1,3 ("1,1-dimethylisoprene").³⁷¹ Heating with sodium or potassium at 125° gave similar results.³⁷¹ Since sodium converts 4,4-dimethylpentadiene-1,2 into the sodium derivative of 4,4-dimethylpentyne-1, the formation of this alkali-metal derivative from 2,4-dimethylpentadiene-2,3 is to be considered. An improbable "left-shift" of equilibrium beyond the unobserved reversion into 4,4-dimethylpentadiene-1,2 would be required.

3-Ethylpentadiene-1,2 (unsym-diethylallene), when heated, gave 3-ethylpentadiene-1,3 and polymers.³⁷¹ With sodium, it formed the sodium derivative of 3-ethylpentyne-1:³⁷¹



The experimental data on the isomerization of allenic alkadienes are given in Table 11, p. 268.

Conclusions

1. Allenic alkadienes isomerize by formation of an alkyne or a conjugated alkadiene.

2. Catalysts for the formation of an alkyne are alcoholic potash, "Floridin," quinoline hydrobromide, sodamide, and sodium metal.

3. Alumina, "Floridin," quinoline hydrobromide, and heat alone are used in isomerizations yielding conjugated alkadienes.

Non-Allenic Alkadienes

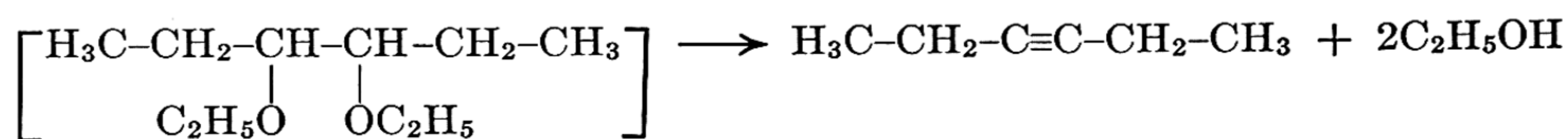
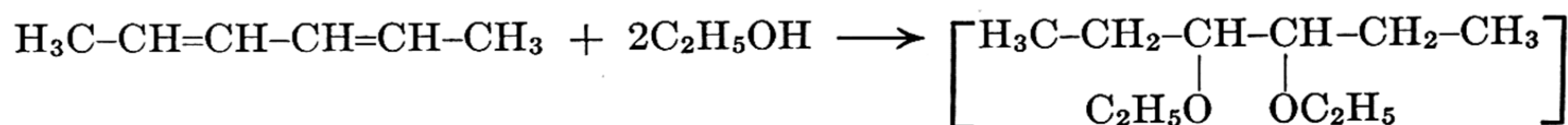
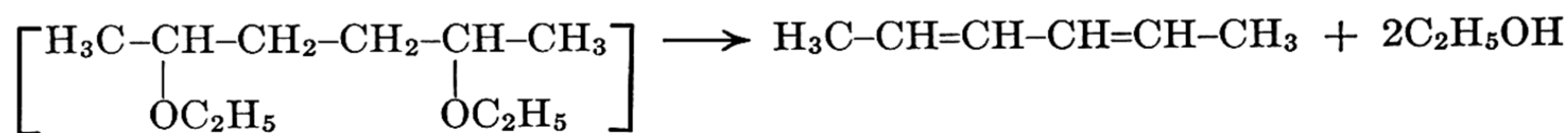
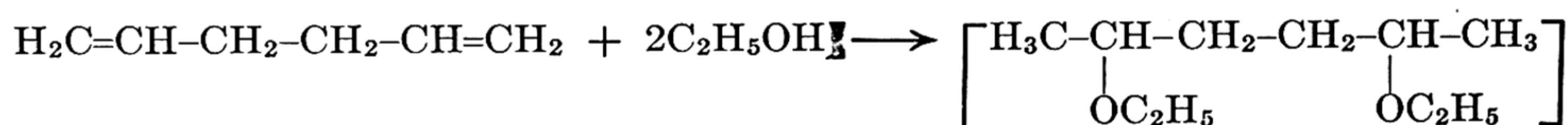
Some work has been carried out on the isomerization of non-allenic alkadienes. Isomerization²⁰⁴ of 2-methylbutadiene-1,3 into 3-methylbutadiene-1,2, by heating with weak alcoholic hydrochloric acid, could not be duplicated by another experimenter.³²⁵ The available data indicate that the process gives 3-chloro-3-methylbutene-1, instead of an isomeric hydrocarbon.

Hexadiene-1,4 (*i.e.*, allylpropenyl) gave hexadiene-2,4 (*i.e.*, dipropenyl) when heated at 100° for 6 hours with concentrated alcoholic potash.²³¹

Hexadiene-1,5 (*i.e.*, diallyl) upon passage through a "Pyrex" vessel at 500°, with carbon dioxide as diluent, probably gave some hexadiene-1,4 and hexadiene-2,4.^{261, 262} Hexadiene-1,5 was 10 per cent isomerized

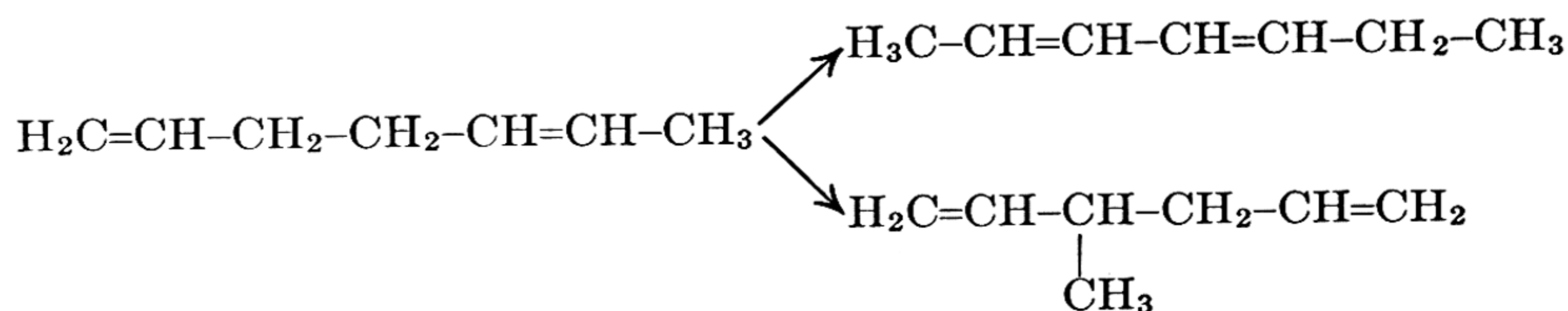
when heated at 250° for 10 days.³³¹ Six passes of hexadiene-1,5 over "Floridin" at 225° yielded 41.5 per cent of hexadiene-2,4.³³³ A 73.4 per cent yield of hexadiene-2,4 was obtained by passage of hexadiene-1,5 with carbon dioxide over palladium-asbestos at 200°, then over platinized carbon at 200°, and again at 300°. ³³⁷ Alumina, as catalyst, converted hexadiene-1,5 into 69 per cent of hexadiene-2,4 at 300° and into 83 per cent at 360°. ³³⁸ Hexadiene-1,5 yielded 3 per cent of hexadiene-1,3 and 39 per cent of hexadiene-2,4 when subjected to alumina at 365°. ^{593a} Chromia effected an isomerization to hexadiene-2,4, which increased from 14.3 per cent at 225° under high feed velocity to 60.9 per cent at 275° and moderate feed velocity. ³⁴³

Hexadiene-1,5, heated 6 hours at 170° with alcoholic potash, gave hexadiene-2,4 and probably some hexyne-3. ¹⁷⁹ The reaction is incomplete, since the product formed contained unchanged diallyl. The following equations are proposed as an explanation of the formation of hexyne-3 (the catalyst is probably C₂H₅OK):



Hexadiene-2,4, when passed over alumina at 360°, gave about 15 per cent of hexadiene-1,3 and 2 per cent of hexadiene-1,4; elevation of temperature to 450-480° resulted in a ten-fold increase in the amount of hexadiene-1,4, together with the formation of pentadiene-1,3 as a new product. ⁴⁴⁵

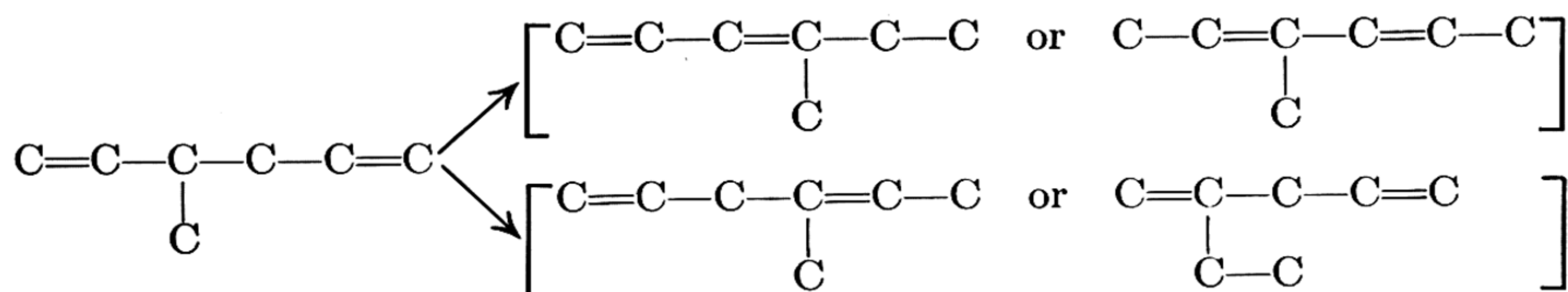
Heptadiene-1,5 was transformed into 6 per cent of heptadiene-2,4 and 8 per cent of 3-methylhexadiene-1,5 by a single passage over alumina at 365°. ^{593a} These isomerizations proceed respectively by migrations of 2 hydrogen atoms (from 3-position into 1-position and from 4-position into 2- or 6-position, referred to the initial chain) and by transfer of a hydrogen atom for a methyl group:



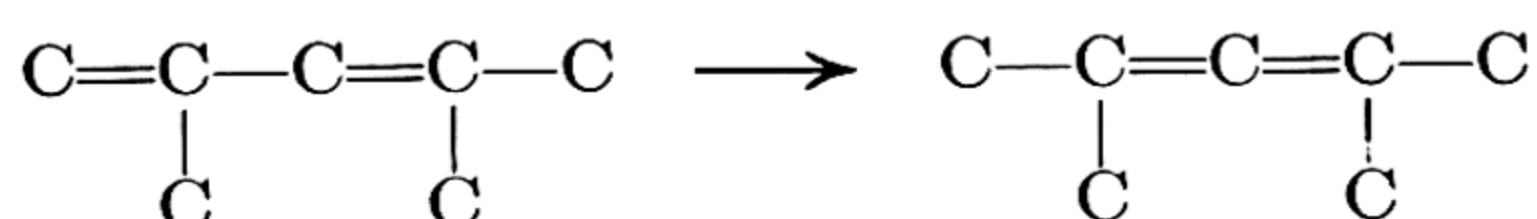
2-Methylhexadiene-1,5 yielded 58 per cent of 2-methylhexadiene-2,4 when passed once over alumina at 365° .^{593a} In this example, both double bonds shift toward a conjugated position, and the final molecule acquires a more stable, terminal isopropylidene, structure (analogous to "trimethylethylene"):



3-Methylhexadiene-1,5 was isomerized both to conjugated and non-conjugated isomers upon passage over alumina at 365° .^{593a} The conjugated isomer (14 per cent) was either 4-methylhexadiene-1,3 or 3-methylhexadiene-2,4, whereas the non-conjugated product (18 per cent) was either 4-methylhexadiene-1,4 or 2-ethylpentadiene-1,4. These products involved the shift of one or both double bonds; the initial carbon chain remained intact:

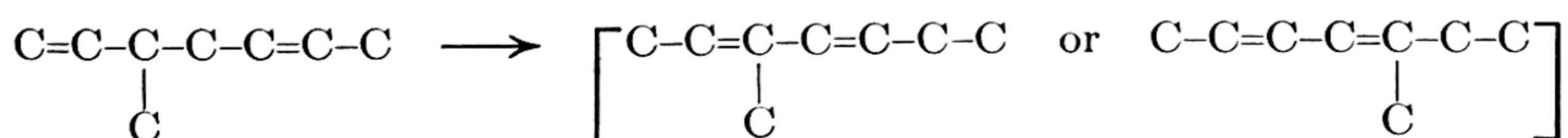


2,4-Dimethylpentadiene-1,3, when passed over "Floridin" at 204° ⁵⁵¹ or $230-235^{\circ}$,⁵⁵³ isomerized into 2,4-dimethylpentadiene-2,3 (*i.e.*, tetramethylallene). In this reaction, a double bond shifts toward the center of the molecule:

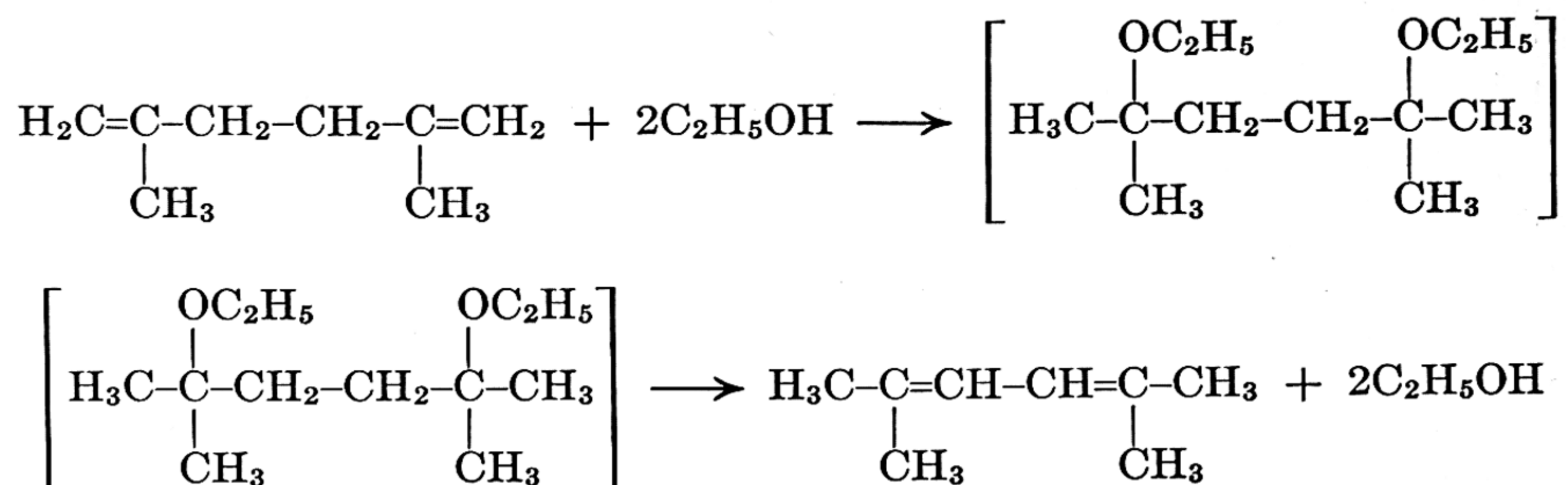


Octadiene-2,6 probably yielded a small quantity of octadiene-3,5 when conducted over alumina at 365° .^{593a} The product contained 72 per cent of unconverted octadiene-2,6.

3-Methylheptadiene-1,5 gave 4 per cent of an isomer, which was either 3- or 5-methylheptadiene-2,4, upon a single passage over alumina at 365° .^{593a} These products would involve the shift of both or only one double bond, respectively:

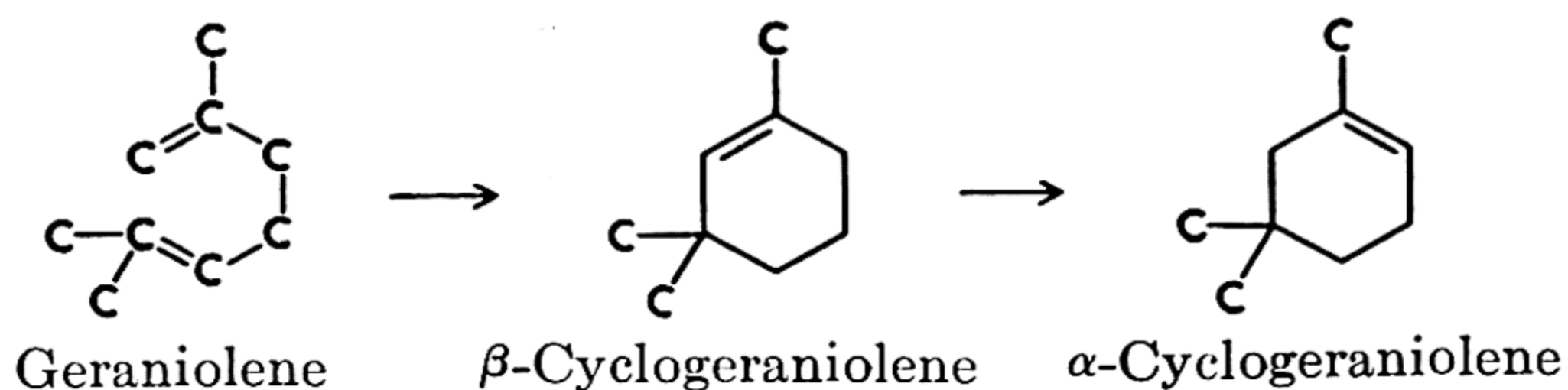


2,5-Dimethylhexadiene-1,5 (*i.e.*, diisobutenyl), when heated at 180° for 4 hours with alcoholic potash, gave unchanged diisobutenyl and 2,5-dimethylhexadiene-2,4 (*i.e.*, diisocrotyl),¹⁷⁹ the last substance representing a shift of 2 double bonds toward the center of the molecule. The reaction was interpreted as follows:

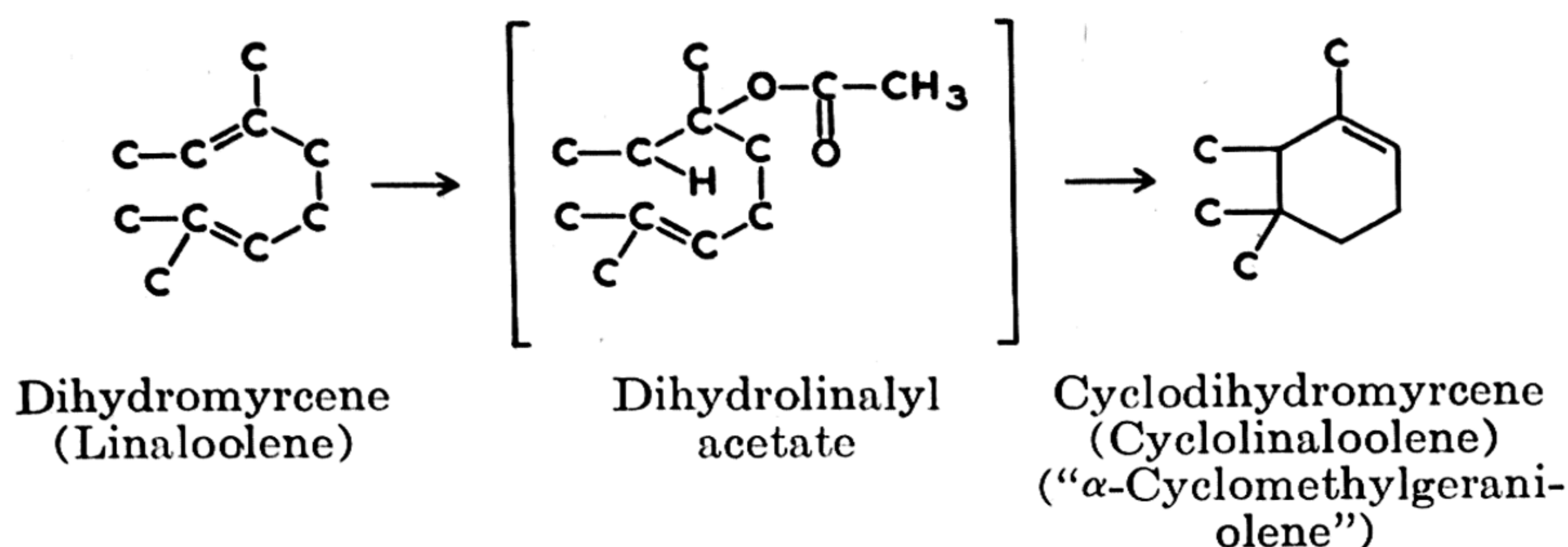


2,5-Dimethylhexadiene-1,5, when passed once over "Floridin" at 205-210°, gave 70 per cent of 2,5-dimethylhexadiene-2,4.³³³ Alumina is a catalyst at 220-225° for the same reaction.³³⁸ An 81 per cent yield of 2,5-dimethylhexadiene-2,4 is readily obtainable from 2,5-dimethylhexadiene-1,5 upon passage over alumina at 365°. ^{593a} Other, less efficient catalysts may be employed, *e.g.*, ferric chloride, magnesium chloride, or potassium hydroxide. The isomerization proceeds slowly at the ebullition point, 114.4°, in an uncatalyzed system.^{593a}

From the foregoing experiments, it is evident that non-conjugated alkadienes exhibit a tendency to conjugate. Cyclization, which is a type of isomerization due to an intramolecular alkylation, may occur in the presence of acidic catalysts. 2,6-Dimethylheptadiene-1,5 (geraniolene), upon contact with 65-per cent sulfuric acid for 3 days,⁵⁸² or when heated at 100° for 4 hours with 60-per cent sulfuric acid,⁵⁸³ undergoes a cyclization into the isomers, α - and β -cyclogeraniolene. These isomerizations are largely controlled by temperature, since considerable loss by resinification occurs with sulfuric acid (sp. gr. 1.56) at temperatures above 15°. ⁶³² α -Cyclogeraniolene is the principal component of the isomeric mixture:⁶³²



2,6-Dimethyloctadiene-2,6 ^{167, 168} probably represents the structure of both Semmler's linaloolene ⁵³¹ and dihydromyrcene. ⁵³² These substances undergo cyclization when treated with acids. Linaloolene heated 20 minutes at 100° with concentrated sulfuric acid gave cyclolinaloolene, ⁵³¹ whereas dihydromyrcene, when treated with acetic acid plus sulfuric acid, gave cyclodihydromyrcene. ^{147, 515, 532} From the proposed structures of cyclodihydromyrcene ^{147, 532} and that of the intermediate dihydrolinalyl acetate, ⁵¹⁵ the last reaction can be expressed as follows:



This reaction should be reinvestigated in order to determine: (a) the extent to which acetic acid acts as a solvent; (b) the extent to which sulfuric acid enters into sulfate formation, and (c) the mechanism of ring closure in alkadienes of this type.

Experimental data on the isomerization of non-allenic alkadienes are given in Table 12, p. 274.

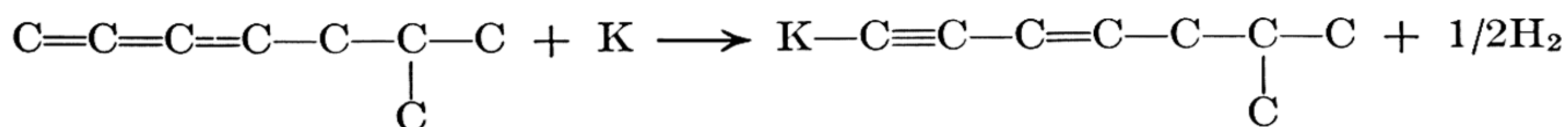
Conclusions

1. Non-allenic alkadienes generally isomerize by a shifting of the double bonds into closer positions (allenic and conjugated).
2. Alumina, "Floridin," and alcoholic potash are typical catalysts for shifting the double bonds of non-allenic alkadienes.
3. Cyclization is the result of treatment with sulfuric acid.

ALKAPOLYENES

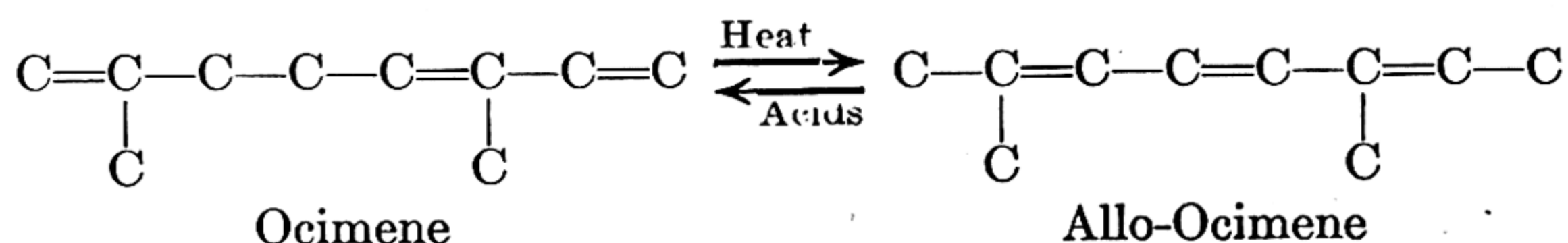
Isomerizations

6-Methylheptatriene-1,2,3, when heated at 110-120° with potassium, gave the potassium derivative of 6-methylhepten-3-yne-1, together with hydrogen:²²⁷

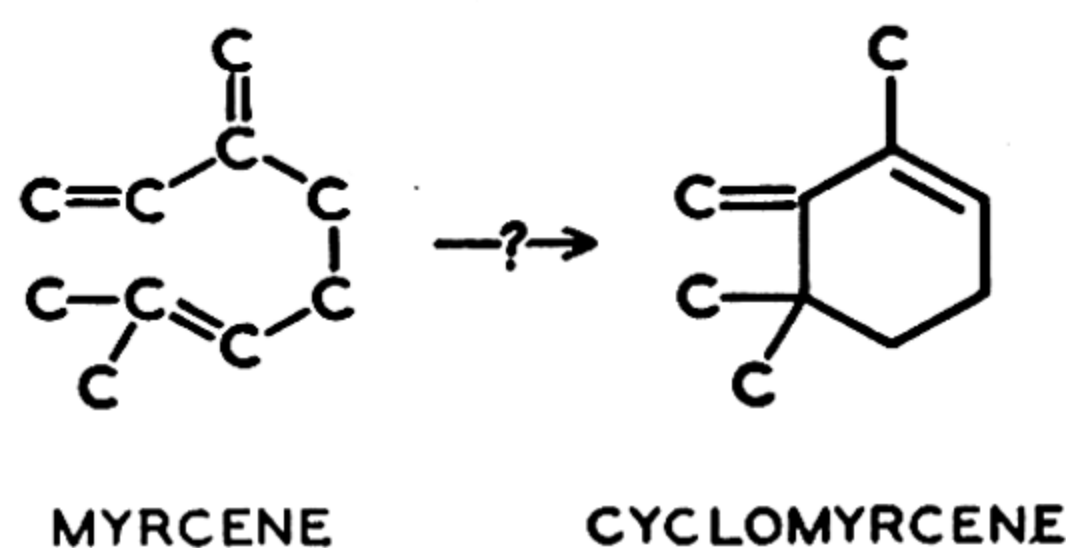


2,6-Dimethyloctatriene-1,5,7 (the acyclic terpene, ocimene), while heated under reflux for nearly 4 hours, formed 82 per cent of a conjugated isomer, 2,6-dimethyloctatriene-2,4,6 (allo-ocimene).¹⁶⁷

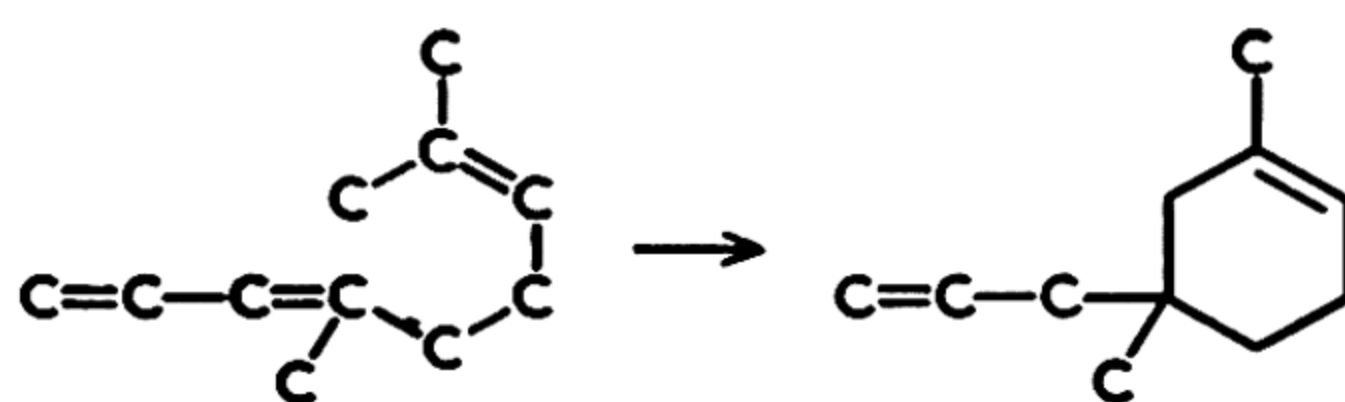
2,6-Dimethyloctatriene-2,4,6 (the acyclic terpene, allo-ocimene), when treated with glacial acetic acid containing sulfuric acid, was re-formed very rapidly, though incompletely, into 2,6-dimethyloctatriene-1,5,7 (ocimene).^{167, 169} This reaction was accompanied by polymerization. Allo-ocimene, upon being heated alone for one hour at 250-300° and then for 0.5 hour at 320°, was converted into an isomeric terpene (23.8 per cent) and polymers (38 per cent).⁸



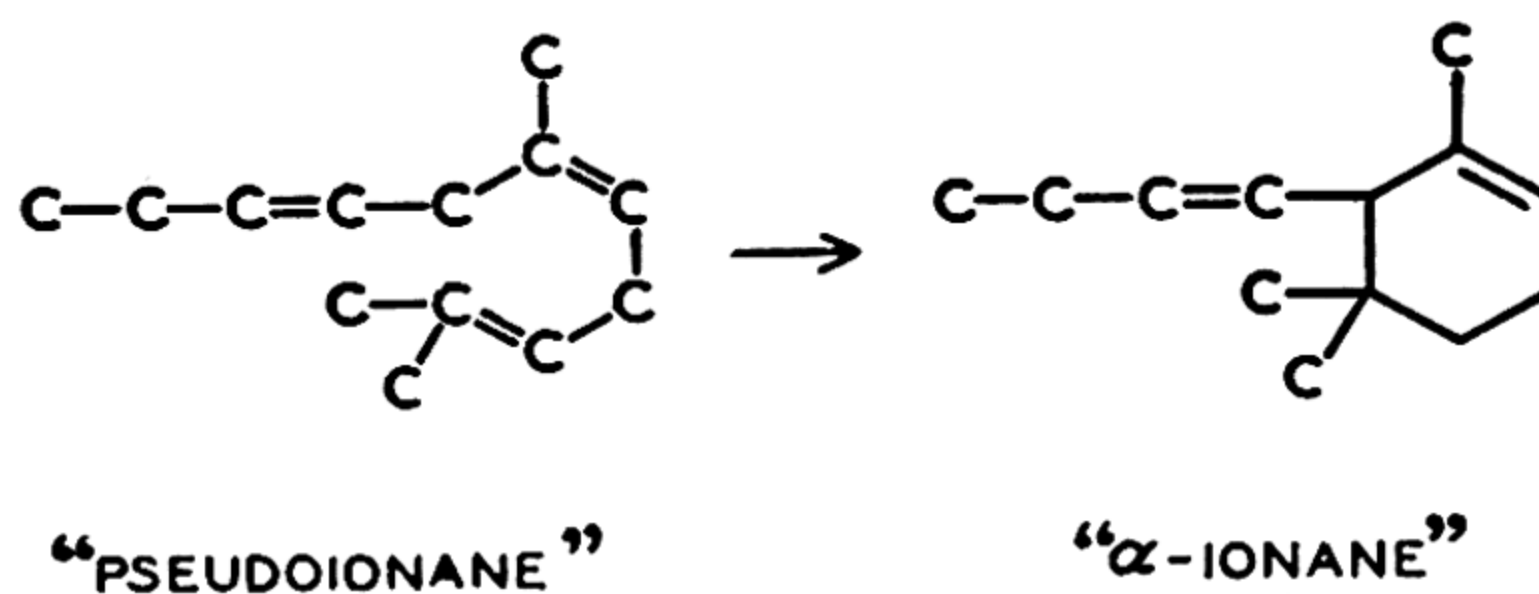
3-Methylene-7-methyloctadiene-1,6 (the acyclic terpene, myrcene), when heated at 300° for 4 hours, gave polymyrcenes and probably cyclo-myrcene:²⁴³



4,8-Dimethylnonatriene-1,3,7, when treated with 80-per cent sulfuric acid, was cyclized into 1,5-dimethyl-5-allylcyclohexene-1:²²⁶

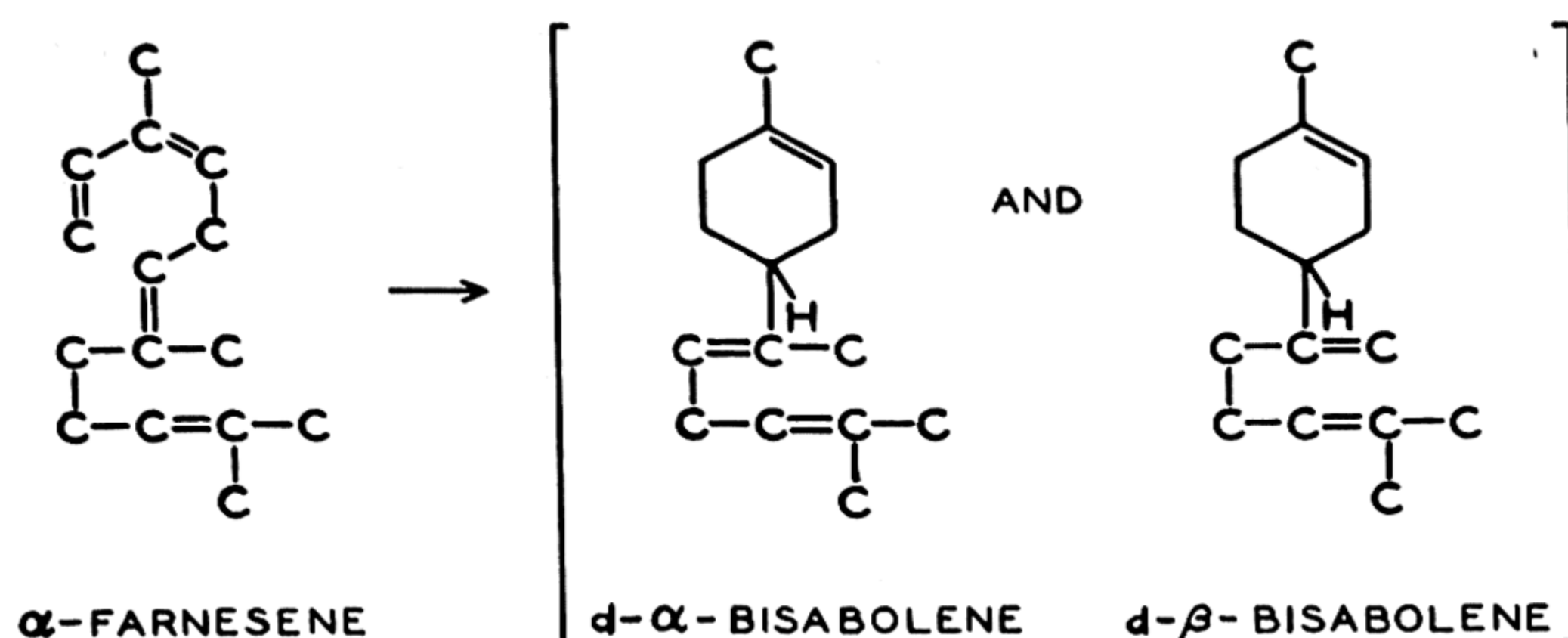


2,6-Dimethylundecatriene-2,5,8 ("pseudoionane") upon being heated with acetic acid containing 2.5 per cent of sulfuric acid, formed 1,5,5-trimethyl-6-(1-butenyl)cyclohexene-1 ("α-ionane"):³⁰⁴



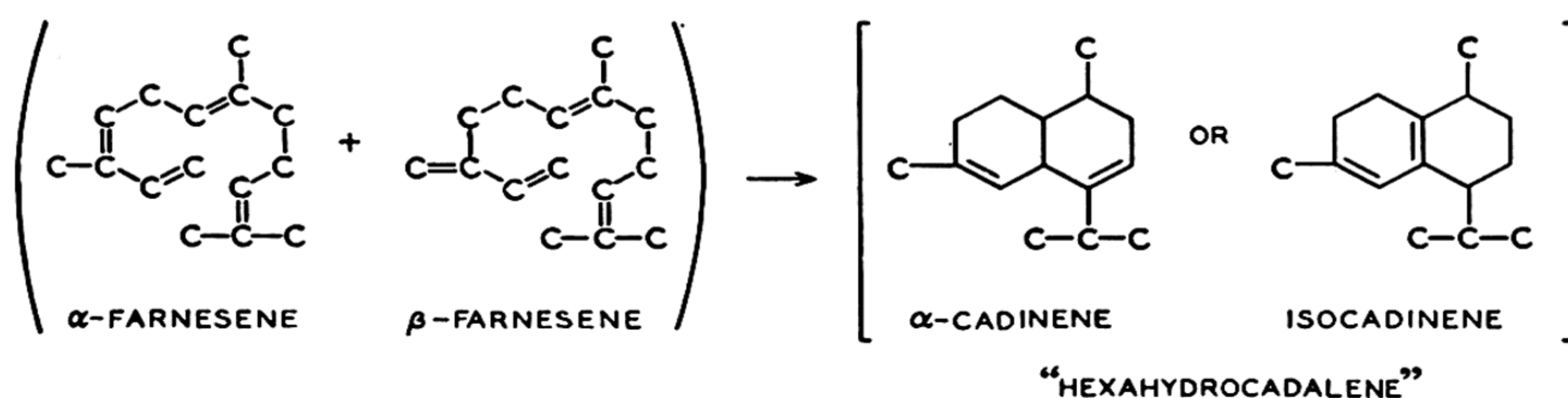
Treatment of the slightly optically active aliphatic sesquiterpene "sesquicitronellene" (from Java citronella oil) with formic acid gave a strongly dextrorotatory cyclic product: "cyclosesquicitronellene."⁵³⁹ This reaction is stated to be an isomerization of farnesene into bisabolene,⁴⁸⁶ and may be interpreted as the conversion of 3,7,11-trimethyldodecatetraene-1,3,6,10 (α-farnesene) into *d*-α- and *d*-β-bisabolenes (the "*d*-limonene of the sesquiterpenes"):^{*}

* Throughout the text and tables of this book, care has been exercised in using configurational notations; the lower-case letters *d*- and *l*- denote discriminately the actual optical rotations of isomers.



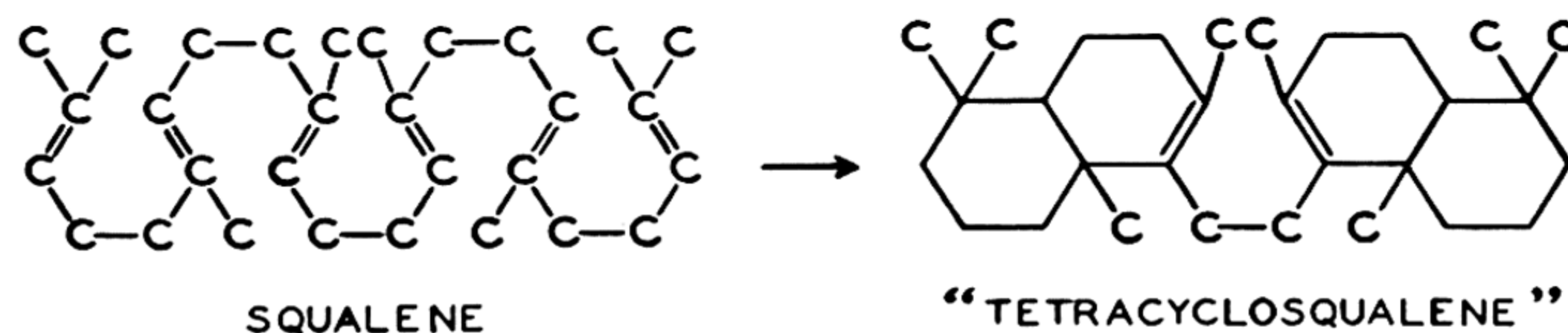
The actual course of this isomerization is unusual in that the formation of d -rotatory bisabolenes predominates.

A mixture of α - and β -farnesenes, when treated with acetic acid containing sulfuric acid, formed a hexahydrocadalene and α -bisabolyl acetate:⁴⁸⁶



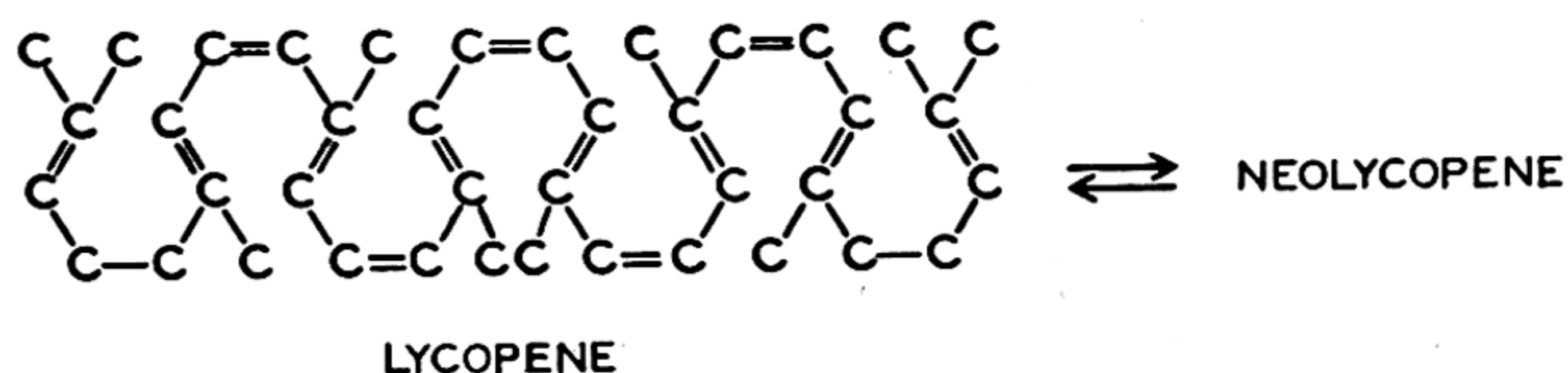
Treatment of a similar α - and β -farnesene mixture with 90-per cent formic acid at 120° gave a monocyclic sesquiterpene product of low optical activity, probably a mixture of α - and β -bisabolenes.⁴⁸²

2,6,10,15,19,23 - Hexamethyltetracosahexaene - 2,6,10,14,18,22 (*i. e.*, squalene) underwent multi-cyclization when boiled with 98-per cent formic acid. Isomerizations of squalene for periods of one-half hour, 3 hours, and 3 days yielded "dicyclosqualene," "tricyclosqualene," and "tetracyclosqualene," respectively.²⁴⁴ The action of a mixture of sulfuric acid and acetic anhydride upon squalene, for 2.5 hours under reflux, probably resulted in the formation of "dicyclosqualene;" a corresponding 18-hour reflux with alcoholic sulfuric acid probably gave "tricyclosqualene."²⁴⁴



2,6,10,14,19,23,27,31-Octamethyldotriacontatridecaene - 2,6,8,10,12,14,-16,18,20,22,24,26,30 (*i. e.*, lycopene, $C_{40}H_{56}$) isomerized spontaneously to neolycopene within a few days in the presence of benzene or petroleum

ether as solvents.⁶⁶⁰ The conversion proceeded more rapidly at elevated temperatures. The structure of neolycopene is unknown, but that of lycopene²⁹⁵ is suited preeminently for cyclization:



Iodine in benzene is an effective catalyst at room temperature both for the isomerization of lycopene into neolycopene, and for the reverse reaction.⁶⁶¹ The ease of reversibility of the reaction may indicate a *cis-trans* isomerization rather than a cyclization-decyclization.

The experimental data on isomerization of alkapolyenes are given in Table 13, p. 280.

Conclusions

Alkapolyenes isomerize by transfer of double bonds, conversion of 2 double bonds into a triple bond, and by cyclization or multi-cyclization.

Chapter III

Alkynes, Alkadiynes, and Alkapolyynes

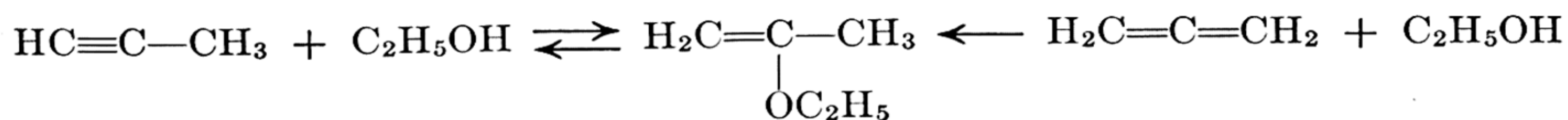
ALKYNES

Isomerizations

The isomerization plus thermolysis of alkynes-1 at 500-600° has been summarized as follows: "At moderate temperatures, polymerization sets in at a rate which must increase with the temperature. At significantly higher threshold temperatures, however, two other effects are noted: (1) partial decomposition into simpler products, and (2) partial isomerization into 1,2-alkadienes. It is noteworthy that the temperature required for the isomerization is about the same as that required for the decomposition into gases."²⁶³

Alkynes, under the influence of alcoholic alkali, undergo isomerization by shifting the position of their triple bond or by forming an allene. Alcoholic potassium hydroxide and alcoholic sodium hydroxide are used interchangeably.¹⁸⁰ Isomerization is possible even among the alkapolyynes, but without the use of alkali.^{132, 499, 563} Thermal and 3-carbon-system isomerizations of alkynes have been discussed in Chapter II under Alkadienes. The number of isomeric alkynes is given in Tables 14 and 15.

Propyne (*i.e.*, methylacetylene or allylene), heated at 170-180° with alcoholic potash for 12 hours, incompletely forms ethyl isopropenyl ether.¹⁷⁸ This ether is stable at 170-180°, whereas ethers from larger alkynes are unstable even at 130-140°. Propadiene (allene) was not reported as a product, which is an unexpected observation, since the same ether is formed *incompletely* from propadiene under similar conditions. The conversion of the ether into allene may be either a very slow reaction or one difficult to effect:



Propyne, upon thermolysis or when treated with alpha particles, is believed to undergo an initial conversion into propadiene.¹⁵⁶ The pyrolysis of propyne at 555° yielded about 14 per cent of hydrocarbons soluble in 82.4-per cent sulfuric acid, besides 28 per cent of liquids taken to be polymers of propadiene.^{370a} The dissolved hydrocarbons were probably

Table 14. Number of Isomeric Hydrocarbons of the Alkyne Series
(Excluding the additional isomers due to stereoisomerism and alkadienes)

From Coffman, Blair, and Henze¹¹⁰

Carbon content	Number of Isomers
2	1
3	1
4	2
5	3
6	7
7	14
8	32
9	72
10	171
11	405
12	989
13	2,426
14	6,045
15	15,167
16	38,422
17	97,925
18	251,275
19	648,061
20	1,679,869
21	4,372,872
22	11,428,365
23	29,972,078
24	78,859,809
25	208,094,977
26	550,603,722
27	1,460,457,242
28	3,882,682,803
29	10,344,102,122
30	27,612,603,765

propadiene with a little propene. Propyne passed over "Floridin" at 180-363°, gave propadiene and polymers.⁵⁵²

Butyne-1 (*i.e.*, ethylacetylene) partially isomerized into butyne-2 (dimethylacetylene) when heated at 170° for 16 hours in the presence of alcoholic potash.^{176, 180} The following equations for the reaction were given;¹⁷⁶ they seem to be correct, with the possible exception of the reaction yielding *free* butadiene-1,2 and effected by free ethanol:

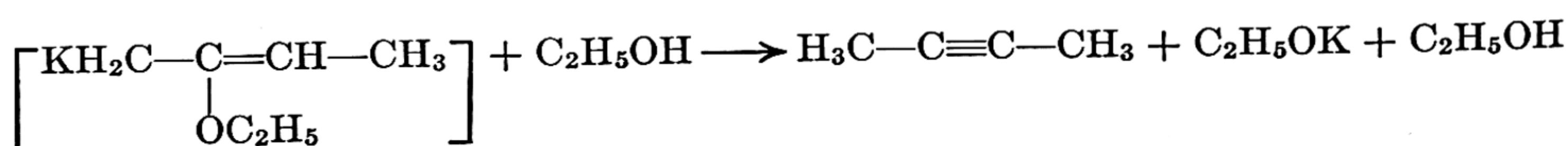
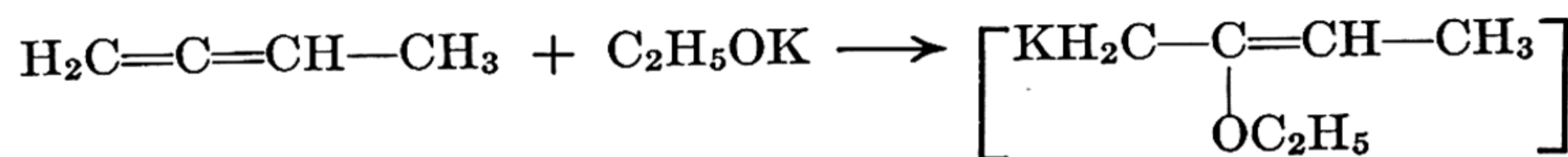
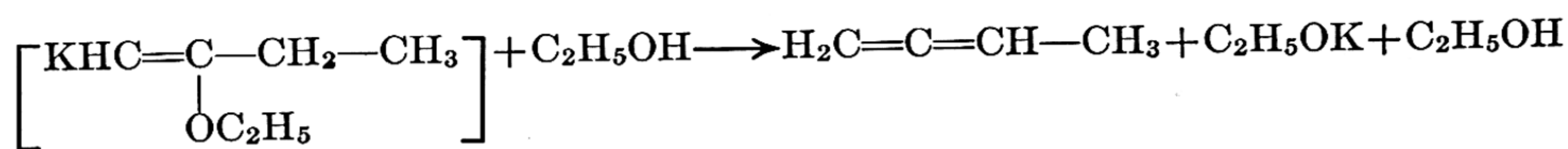
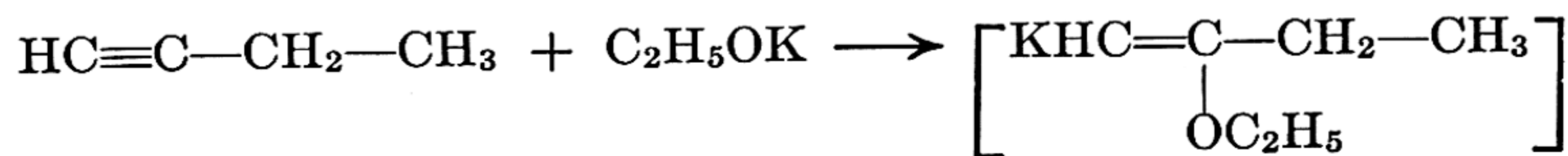


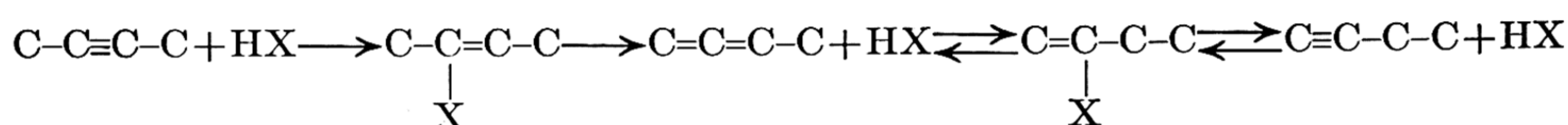
Table 15. Isomeric Alkynes.

Carbon content	RC≡CH		RC≡CR'		RC≡CH and RC≡CR'		Total isomers
	Stereo	Non-stereo	Stereo	Non-stereo	Total stereo	Total Non-stereo	
3	0	1	0	0	0	1	1
4	0	1	0	1	0	2	2
5	0	2	0	1	0	3	3
6	2	3	0	3	2	6	8
7	6	5	2	5	8	10	18
8	20	8	8	11	28	19	47
9	60	14	30	19	90	33	123
10	176	23	101	38	277	61	338
11	512	39	316	68	828	107	935
12	1,488	65	975	129	2,463	194	2,657
13	4,326	110	2,948	232	7,274	342	7,616
14	12,648	184	8,878	428	21,526	612	22,138
15	37,186	310	26,622	768	63,808	1,078	64,886
16	109,980	520	79,980	1,393	189,960	1,913	191,873
17	327,216	876	240,590	2,487	567,806	3,363	571,169
18	979,020	1,471	726,238	4,460	1,705,258	5,931	1,711,189
19	2,944,414	2,475	2,199,070	7,924	5,143,484	10,399	5,153,883
20	8,897,732	4,159	6,683,108	14,095	15,580,840	18,254	15,599,094
21	27,004,290	6,996	20,378,720	24,925	47,383,010	31,921	47,414,931
22	82,287,516	11,759	62,347,546	44,065	144,635,062	55,824	144,690,886

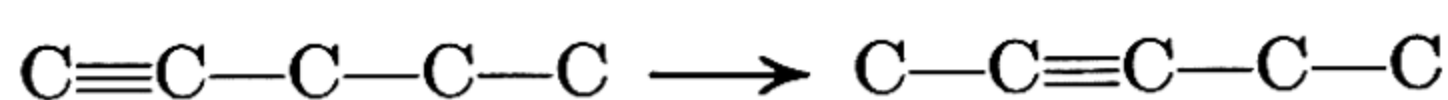
 From Coffman¹⁰⁹

The isomerization of butyne-1 by alcoholic alkali is always incomplete.^{176, 180, 653} There are no indications that isomerizations with such alkali may be reversible. Butyne-1 formed butadiene-1,2 when passed over "Floridin" at 275°. ⁵⁵⁴ However, butadiene-1,3 resulted when pumice was utilized as the catalyst at 300°. ^{141a}

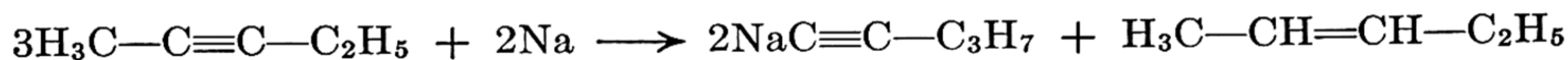
Butyne-2 was isomerized into butadiene-1,2 and butyne-1 upon passage over "Floridin" at 278-285°. ⁵⁵⁴ This reaction is opposite in direction to that observed when alcoholic alkali acts upon butyne-1. Possibly the "Floridin" acts as an "acidic" catalyst temporarily supplying a proton:



Pentyne-1 (propylacetylene), heated 24 hours at 170° with alcoholic potash, gave pentyne-2 (methylethylacetylene).^{176, 180} Isomerization occurred even at 30° or 40°. ¹⁸⁰

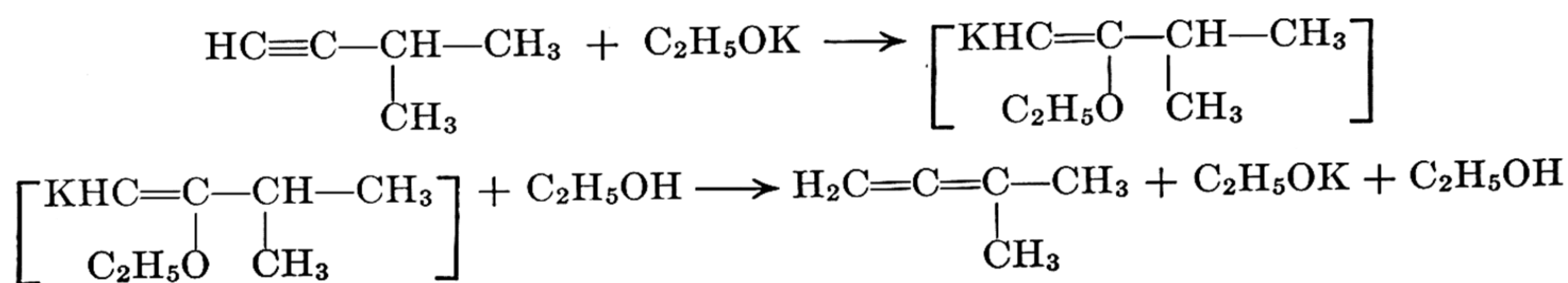


Pentyne-2, when heated for 4-5 hours at 100° with less than one mole portion of sodium, gave the sodium derivative of pentyne-1, hydrolyzed by water to the last alkyne.¹⁷⁷ This reaction, which is opposite in character to that with alcoholic potash, was expressed as follows:

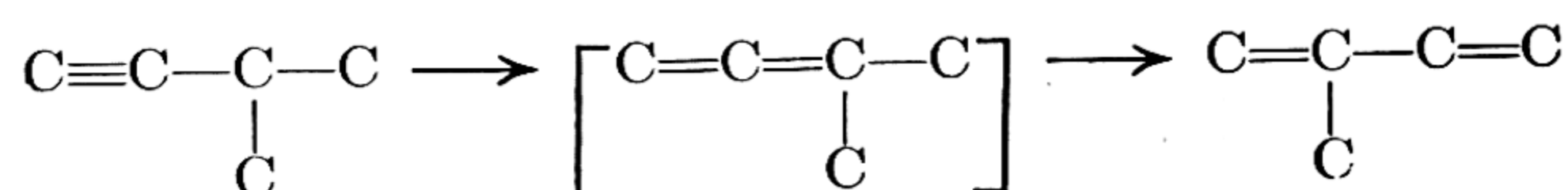


The presence of pentene-2 was not established definitely; its formation accounts for the hydrogen loss in forming the sodium derivative.

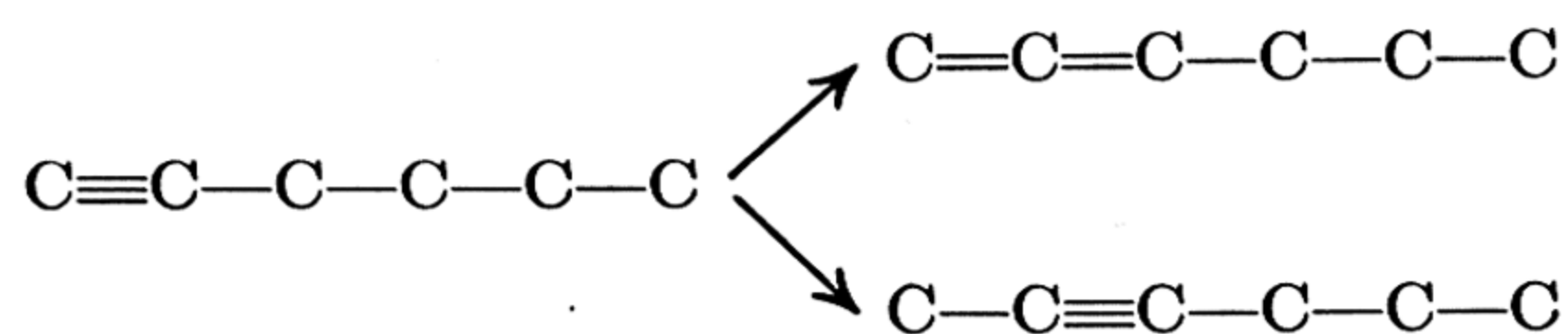
3-Methylbutyne-1 (isopropylacetylene), heated for 6 hours at 150° with alcoholic potash, gave 3-methylbutadiene-1,2 (unsym-dimethylallene).^{176, 180} Increasing the temperature to 170° resulted in polymerization of the allenic alkadiene. The isomerization was explained by two equations:¹⁷⁶



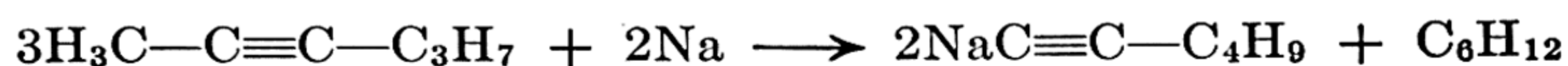
Alumina catalyzed the isomerization of 3-methylbutyne-1 into 2-methylbutadiene-1,3 (isoprene) at 400°, ^{29, 32, 639} which corresponds to the fact that alumina at 300° converted 3-methylbutadiene-1,2 (unsym-dimethylallene) into isoprene.³¹ 3-Methylbutyne-1 and "Floridin" at 270° gave a little 3-methylbutadiene-1,2 and a trace of isoprene.⁵⁴⁸



Heating of hexyne-1 at 500°, 550°, and 600° gave some hexadiene-1,2, and at 600° also a trace of hexyne-2.²⁶³ A partial conversion into decomposition products occurred in all the experiments.

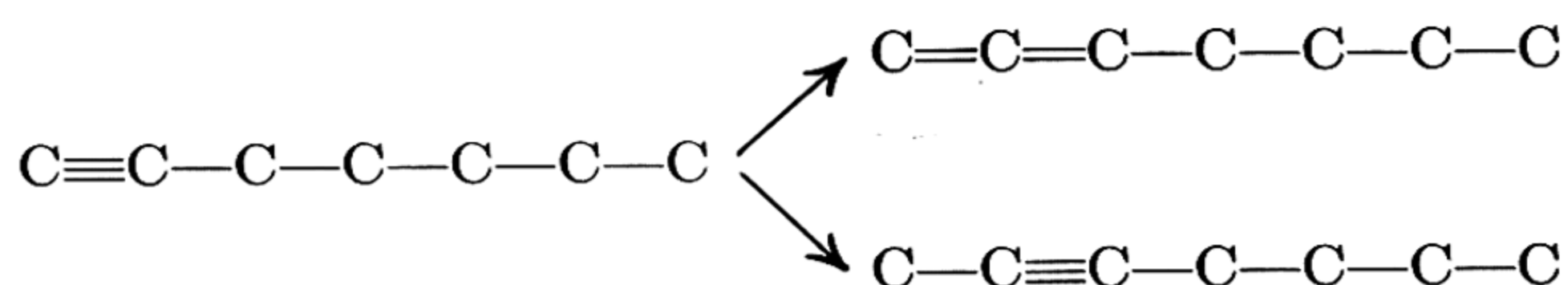


Hexyne-2 (methylpropylacetylene) yielded the sodium derivative of hexyne-1 in the presence of sodium at 150-160°. ¹⁷⁷ The reaction was given as:



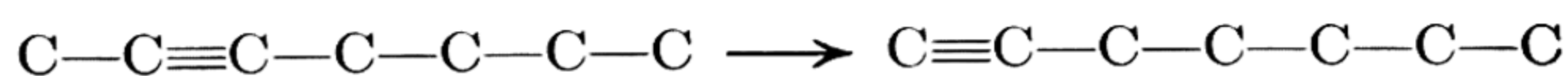
3,3-Dimethylbutyne (*tert*-butylacetylene) did not isomerize even when heated for 16 hours at 200° with alcoholic potash,^{176, 180} a fact that is in agreement with the theory of "the unstable ethyl ether."¹⁷⁶

The isomerization plus thermolysis of heptyne-1 at 600° gave some heptadiene-1,2, a trace of heptyne-2, besides simpler decomposition products.²⁶³ Isomerization of heptyne-1 upon passage over pumice at 350° has been observed also.²³⁴

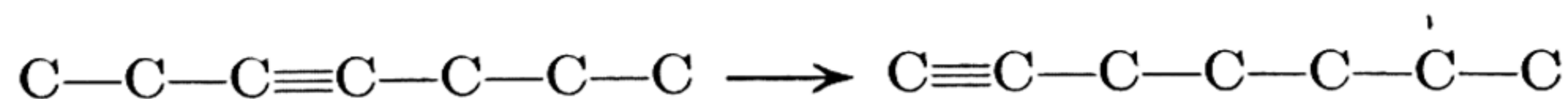


Heptyne-1, heated with alcoholic potash at 140-150° for either 24 hours⁴² or 36 hours,⁴¹ was converted completely into heptyne-2. The isomerization of heptyne-1 (63 per cent preparation) was completed in 5 hours of treatment with potassium hydroxide and alcohol at 200°. ²⁴ Dry soda-lime had no effect on heptyne-1 (76 per cent content, temperatures below 275°, periods up to 5 hours). ²⁴ Passage of heptyne-1 (90 per cent pure) over soda-lime at 380° gave 70 per cent of heptyne-2. ²³⁴

Treatment of heptyne-2 (80 per cent mixture containing some heptyne-1) with sodamide and mineral oil as diluent, at 160° for 12 hours, gave a final product containing 64 per cent of heptyne-1: ²³⁴

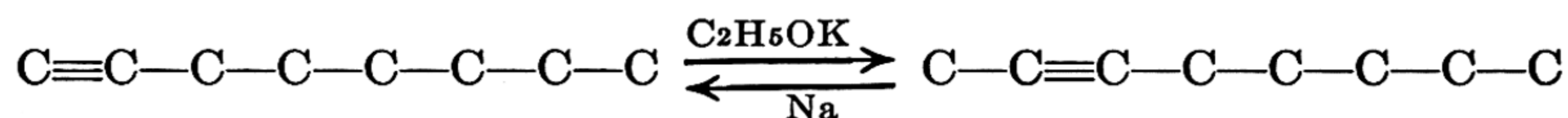


Heptyne-3, when heated for 4 hours at 170° with sodamide and pseudocumene as diluent, formed 70-80 per cent of heptyne-1: ⁸¹

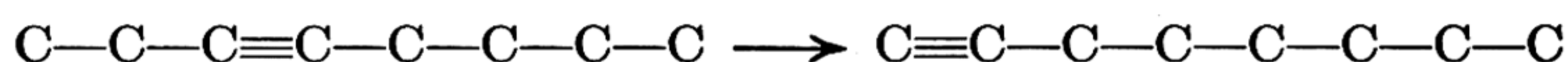


Octyne-1 isomerized completely to octyne-2 when heated for 36 hours at 140-150° with alcoholic potash. ^{41, 42} The reverse reaction takes place with sodium. Octyne-2, heated for 8 hours on a sand bath with sodium, gave a 9 per cent yield of octyne-1 (after regeneration), together with

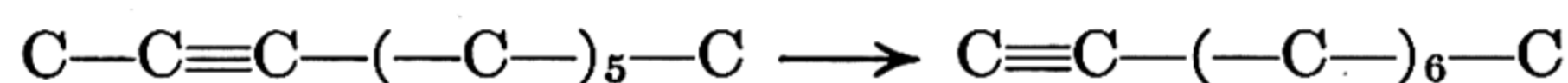
much unconverted octyne-2.¹³⁵ Similarly, octyne-2, heated for 36 hours in a sealed tube with sodium, first upon a water bath and then upon a salt bath, gave a 75 per cent yield of crude octyne-1.⁴³ Octyne-2, when heated for one hour at 150° with sodamide and pseudocumene as diluent, gave 80 per cent of octyne-1.⁸¹



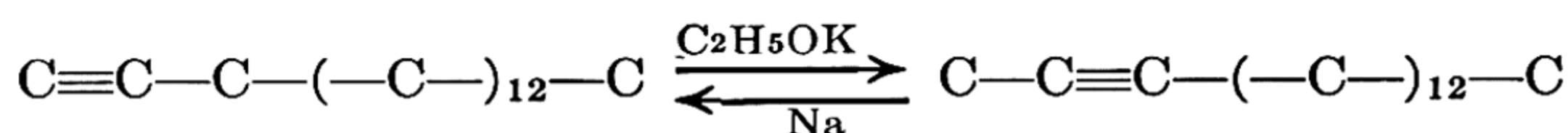
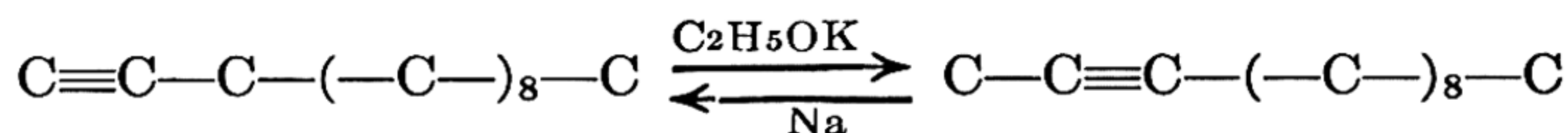
Octyne-3 isomerized into 55 per cent of octyne-1 when heated for 9 hours at 170° with sodamide and petroleum as a diluent:⁸¹



Nonyne-2, heated for 2 hours at 160° with sodamide and petroleum as diluent, gave 83 per cent of nonyne-1.⁸¹



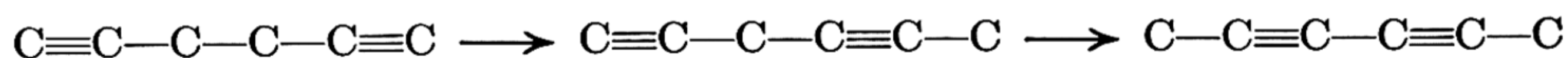
In the study of isomerization of dodecyne-1 and dodecyne-2, and of hexadecyne-1 and hexadecyne-2, it was found that alcoholic potash changed the alkyne-1 to the alkyne-2, whereas sodium brought about the reverse reaction:³²³



Isomerizations

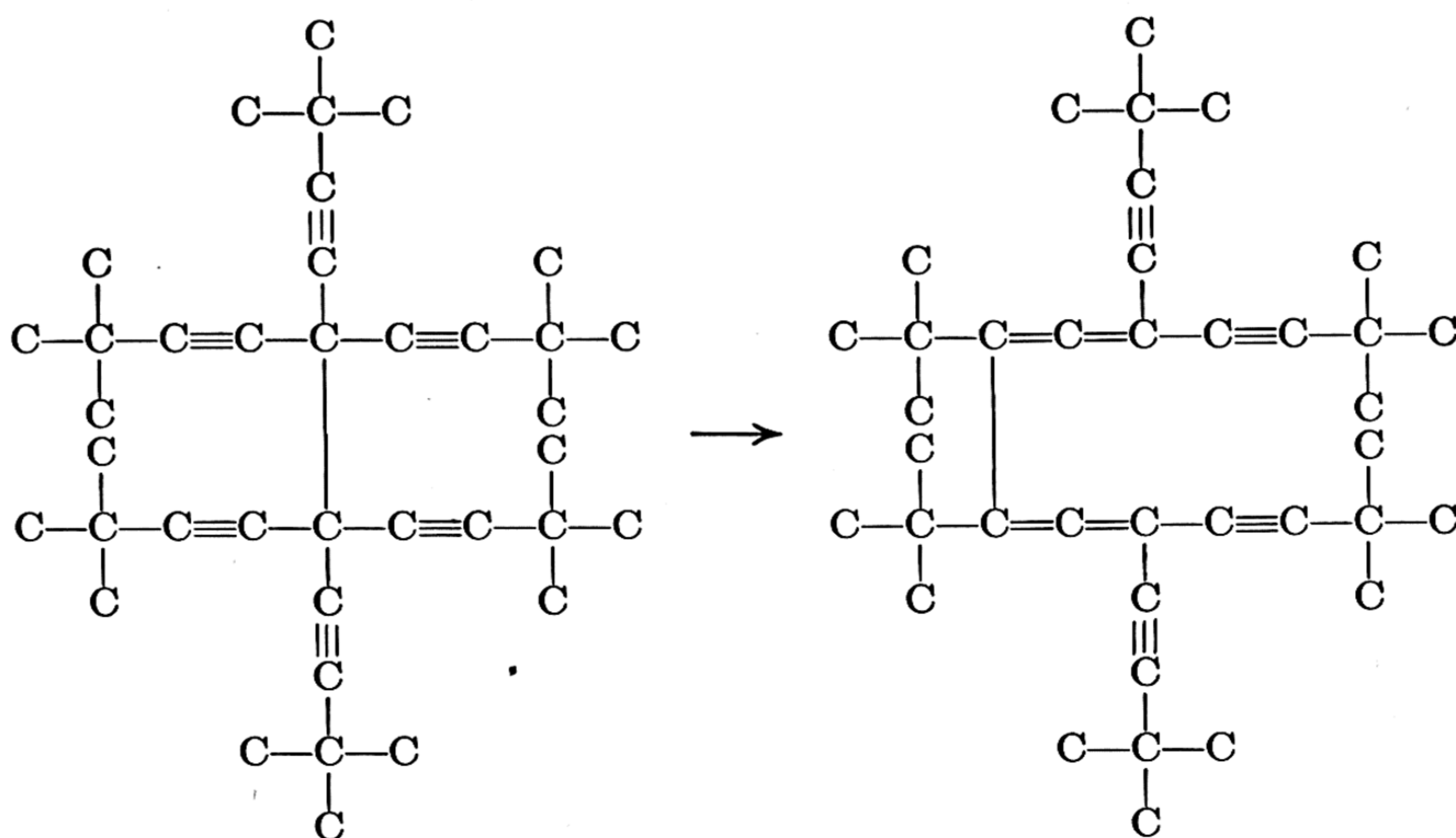
ALKADIYNES AND ALKAPOLYYNES

Alkadiynes. In the isomerization of alkadiynes, hexadiyne-1,4 formed hexadiyne-2,4 when treated repeatedly with alcoholic potash under unspecified conditions.³³⁶ Another observer,²³¹ however, has reported only polymerization by alcoholic potash. Hexadiyne-1,5 (*i.e.*, dipropargyl), heated at 100° for one hour with alcoholic potash, underwent a partial isomerization into hexadiyne-2,4.¹⁷⁹ An unsaturated ether, $\text{C}_8\text{H}_{12}\text{O}$, was isolated;¹⁷⁹ it is probably the intermediate responsible for one step of the isomerization. Pending further investigations, these reactions can be considered as the following right-shift of reactions:

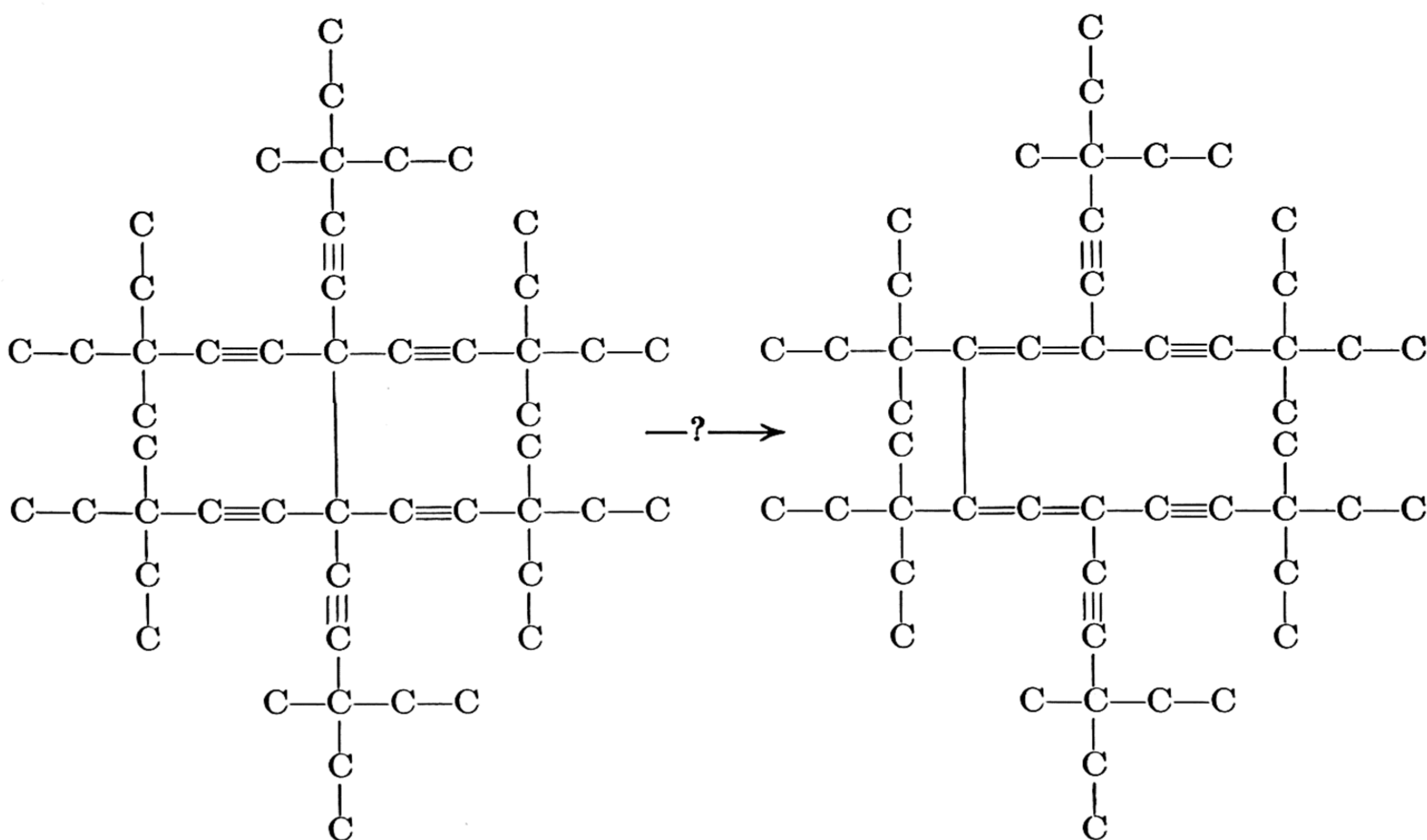


Alkapolyynes. 2,2,9,9-Tetramethyl-5,5,6,6 - tetra-*tert* - butylethynyl-decadiyne-3,7 (*i.e.*, hexa-[*tert*-butylethynyl]-ethane), heated for one hour at 100° in alcoholic solution,⁴⁹⁹ formed an isomer (40-60 per cent) to which has been assigned the diallenyl structure of 2,2,13,13-tetramethyl-5,10-di-*tert*-butylethynyl-7,8 - di - *tert*-butyl - tetradecatetraene - 5,6,8,9-diyne-3,11.⁵⁶³ The same isomer was obtained by heating a xylene solu-

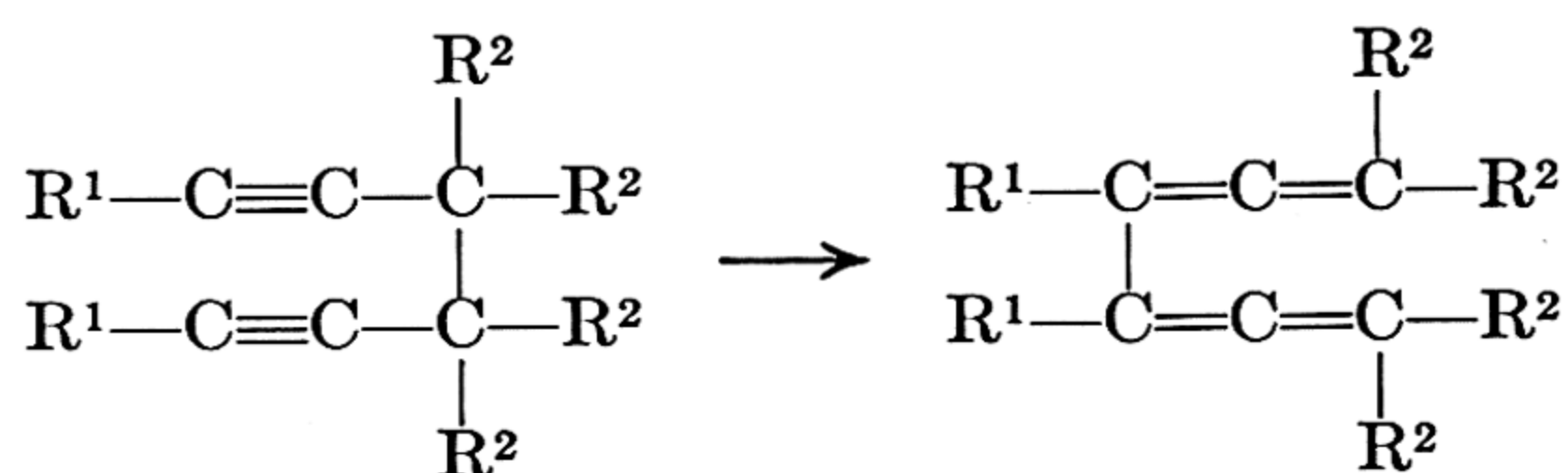
tion⁴⁹⁹ and in an attempted reduction of the "ethane" by hydrogen under pressure at 70-80° in the presence of alcohol and a platinum black plus platinum oxide catalyst:⁵⁷⁵



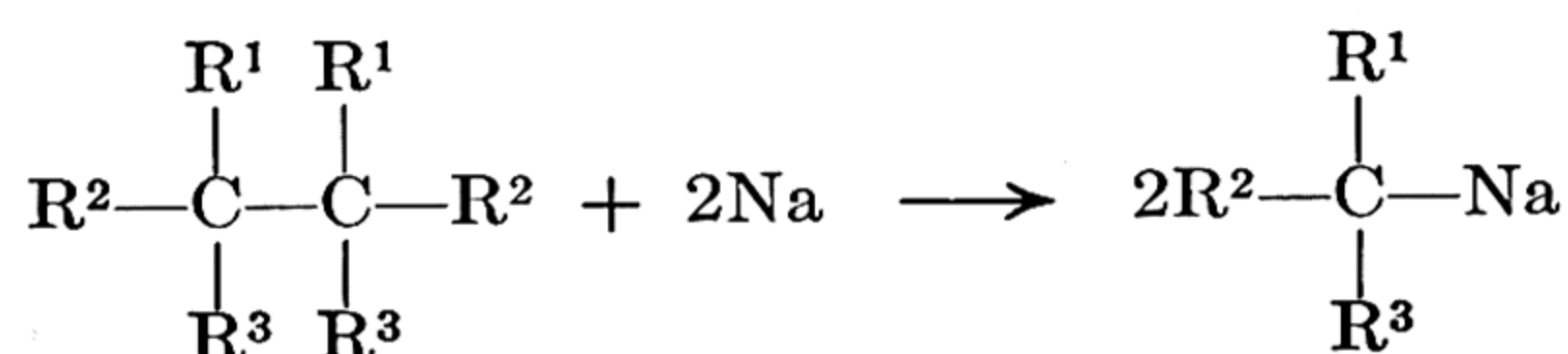
3-10-Dimethyl-3,10-diethyl-6,6,7,7-tetra-(3-methyl-3-ethylpent-1-yn-1-yl)-dodecadiyne-4,8 (*i.e.*, hexa-[3-methyl-3-ethylpent-1-yn-1-yl]-ethane), boiled for one hour in alcoholic solution, gave an isomer,¹³² probably an analogous diallenyl with the structure of 3,14-dimethyl-3,14-diethyl-6,11-di-(3-methyl-3-ethylpent-1-yn-1-yl)-8,9-di-(3-methylpent-3-yl)-hexadecatetraene-6,7,9,10-diyne-4,12:



In the formation of the diallenyl products from the alkynyl hexa-substituted ethanes, there is an isomerization without hydrogen transfer. Apparently, a C—C *break*, and a C—C *union* of 2 *rearranged* free radicals occur as follows:

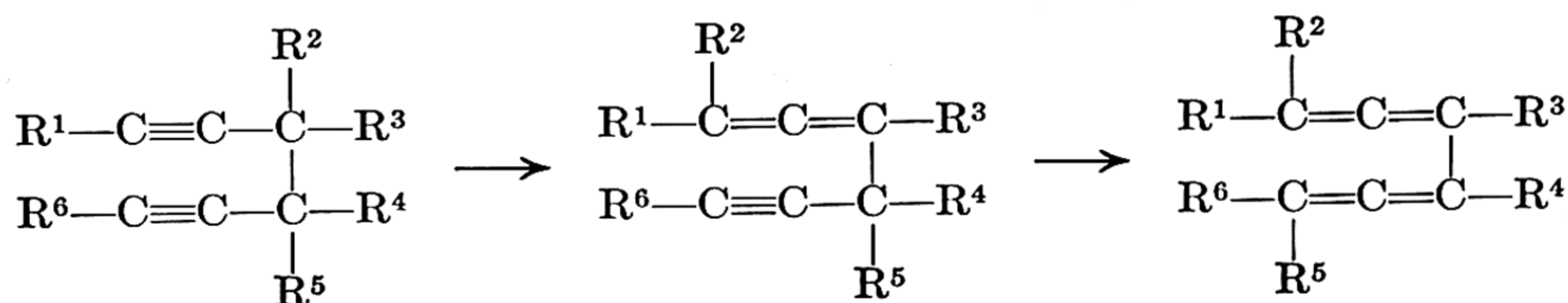


Such an explanation is supported by the observed formation of sodium alkyls upon treatment of the substituted ethanes with sodium amalgam.⁵⁶⁴ An analogous type of reaction will be considered again in Chapter VI.

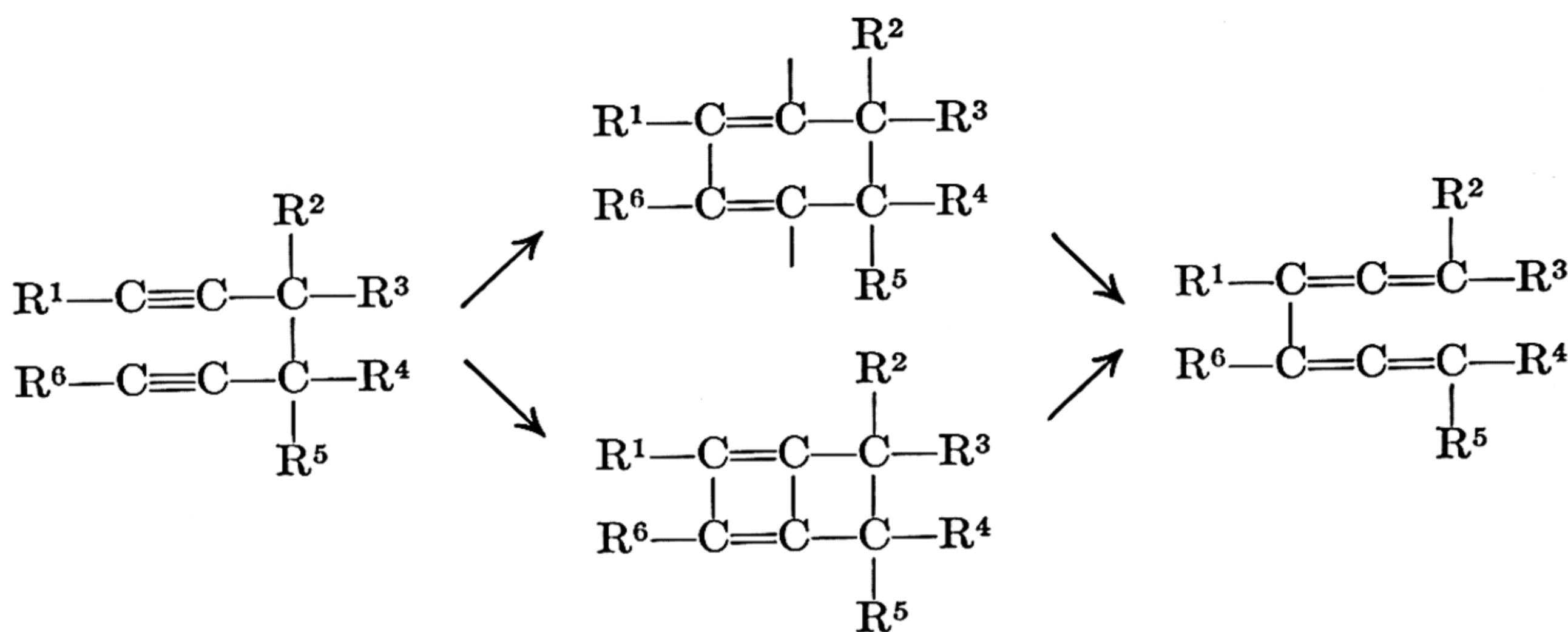


The isomerization mechanism in the alkynyl hexa-substituted ethanes could be clarified by investigating less symmetrical derivatives in the 4 following cases:

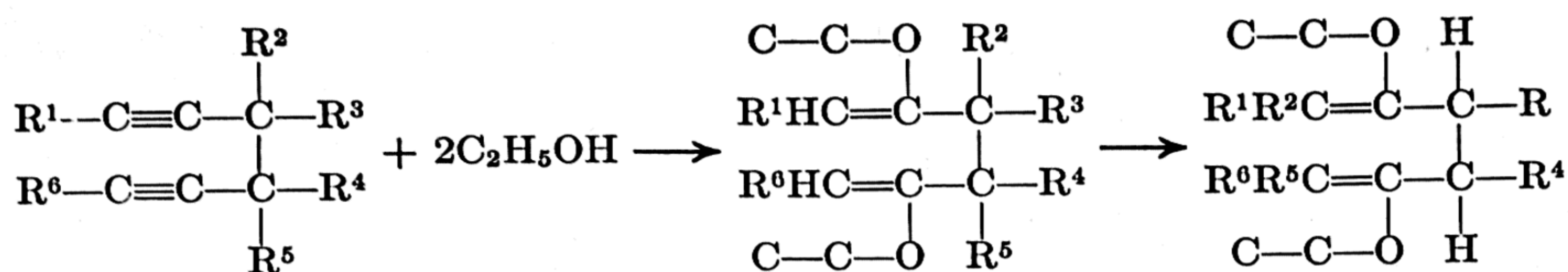
1. An intermediate allene-alkyne formation:



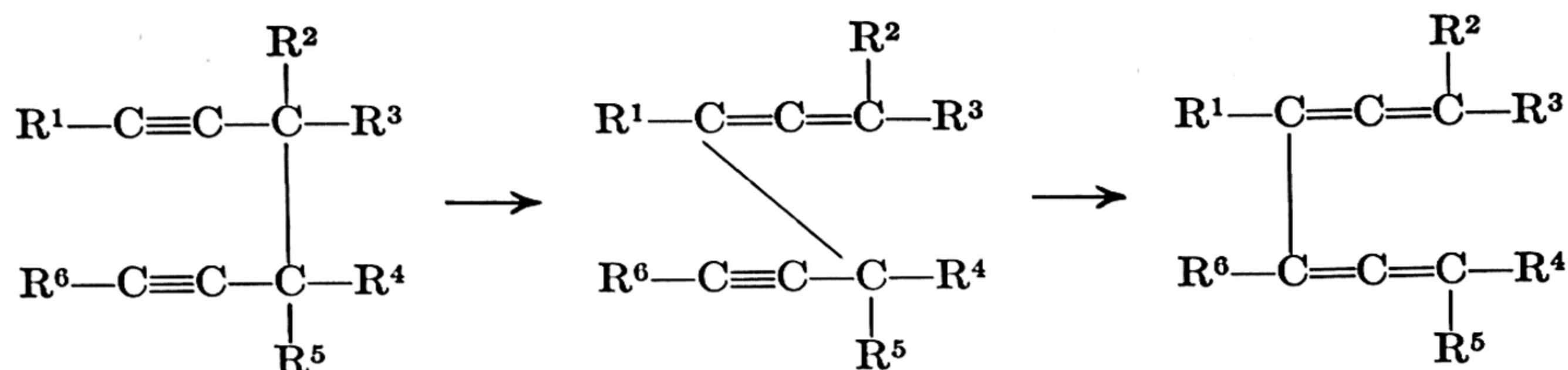
2. An intermediate cyclic- or bicyclic-compound formation:



3. A rearrangement of the two added hydrogen atoms and two R groups in alkenyl ethers:



4. A double "allylic type" of isomerization:⁵⁸¹



The isomerizations of alkynes, alkadiynes, and alkapolyynes are given in Table 16, p. 284.

CONCLUSIONS

1. Isomerizations of alkynes take place only by a shift in position of the triple bond or by its transformation into two double bonds.

2. Alkynes form allenes when heated alone or in the presence of ethanol, alcoholic potash, "floridin," and pumice. Heating with alumina gives a conjugated diene.

3. Alkynes, $\text{H}-\text{C}\equiv\text{C}-\text{R}$, containing a tertiary third-carbon atom can isomerize up to, but not beyond, the allene stage. Alkynes containing a tertiary group R without a labile hydrogen (*i.e.*, a quaternary third-carbon atom) cannot isomerize at all by a hydrogen migration. Two labile hydrogens must be present on the third carbon-atom in order that triple bonds may shift "intact" and isomerize catalytically beyond the allene stage to new alkynes (in agreement with Faworsky's theory).

4. Sodium metal causes an alkyne-2 (methylacetylenes) to become an alkyne-1. Sodamide acts like sodium.* Both reactions probably depend upon a displacement of the equilibrium due to the formation of stable organosodium-compounds. "Floridin" converts an alkyne-2 into an alkyne-1 plus an allene; hence it is a catalyst of "mixed" type.

5. Alcoholic potash and soda-lime cause an alkyne-1 to become an alkyne-2. However, this change occurs at a higher temperature than the reverse isomerization.

6. Unconjugated alkadiynes form a conjugated system of triple bonds when treated with alcoholic potash. This isomerization shifts one

* Free sodium, present at times as an impurity,⁶⁸ may be responsible for the activity of sodamide.

Chapter IV

Cyclanes, Spiranes, Bicyclanes, and Polycyclanes

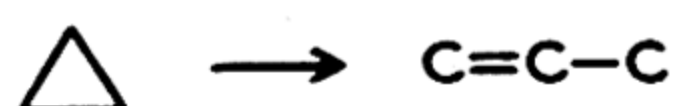
The cyclanes, spiranes, bicyclanes, and polycyclanes are discussed in the order: cyclanes and cyclanes with saturated side-chains, cyclanes with unsaturated side-chains, spiranes, bicyclanes and bicyclanes with saturated side-chains, bicyclanes with unsaturated side-chains, tricyclanes, and pentacyclanes. A tetracyclane has not been isomerized to date, although many interesting cases can be readily conceived.^{353a}

CYCLANES AND CYCLANES WITH SATURATED SIDE-CHAINS

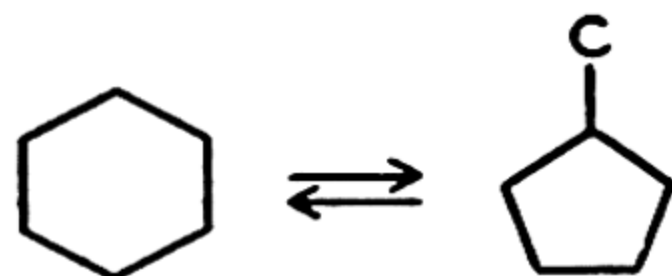
Mechanism

The isomerization of cyclanes (monocycloparaffins), with saturated side-chains or without side-chains, may proceed *theoretically* in 8 different directions:

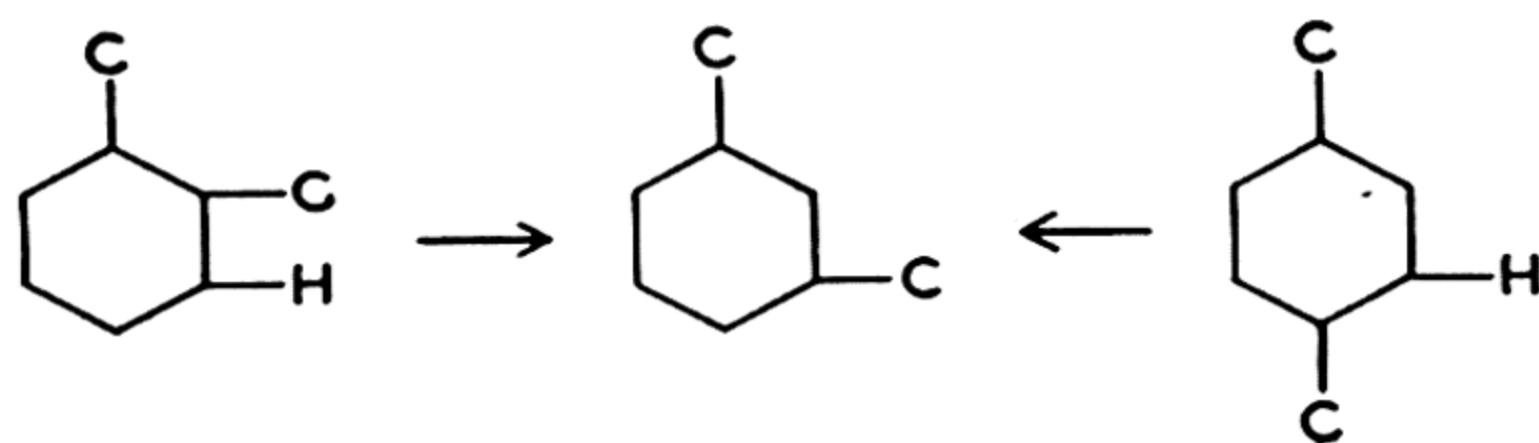
1. Rupture of the ring and formation of an alkene. This requires (over-all) a C—C and a C—H *break*, a C—C *union* to form a double bond, and a new C—H *tie*. This can be illustrated by the known reaction:



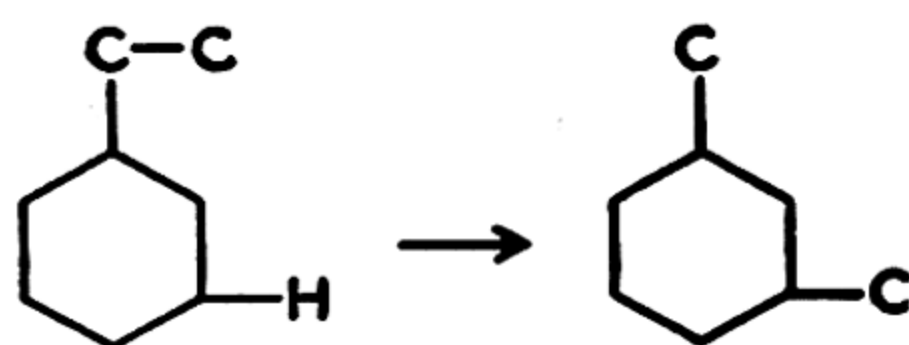
2. Change of the ring size. In its over-all aspect, this change requires a C—C and a C—H break, with subsequent recombination in new directions. This can be described by an established equilibrium:



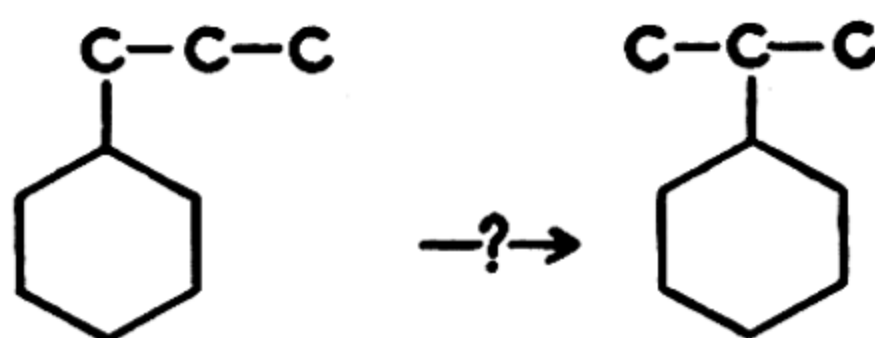
3. Shift of intact side-chains along the ring. This proceeds (over-all) by a dehydrogenation (one hydrogen atom only at the ring) plus dealkylation and a subsequent alkylation plus hydrogenation. An exchange in the position of alkyl and hydrogen occurs, as in the known reactions:



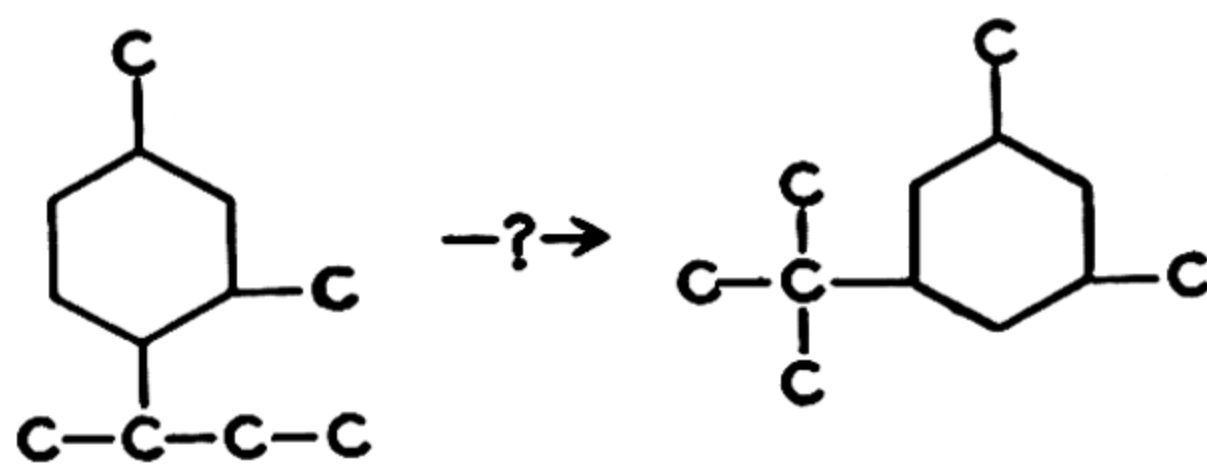
4. Isomerization by rupture within the side-chain, followed by an attachment of the one or more resulting new radicals along the ring. The over-all changes involved are dehydrogenation (usually of only one hydrogen atom at the ring) plus scission within the side-chain, followed by alkylation plus hydrogenation. The following observed reaction is characteristic of these changes:



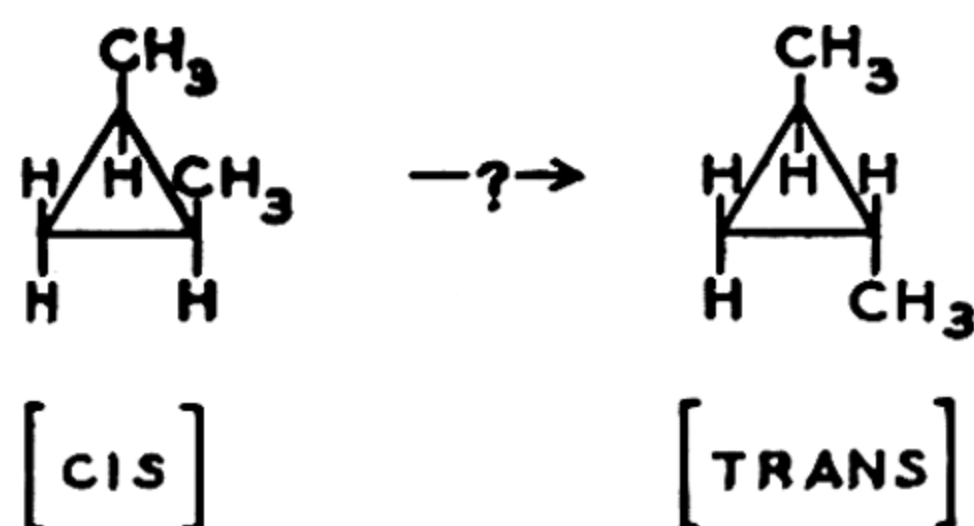
5. Isomerization of the side-chain itself, consisting of ruptures therein and the formation of a more symmetrical side-chain. This change has not been observed in the cyclanes to date.



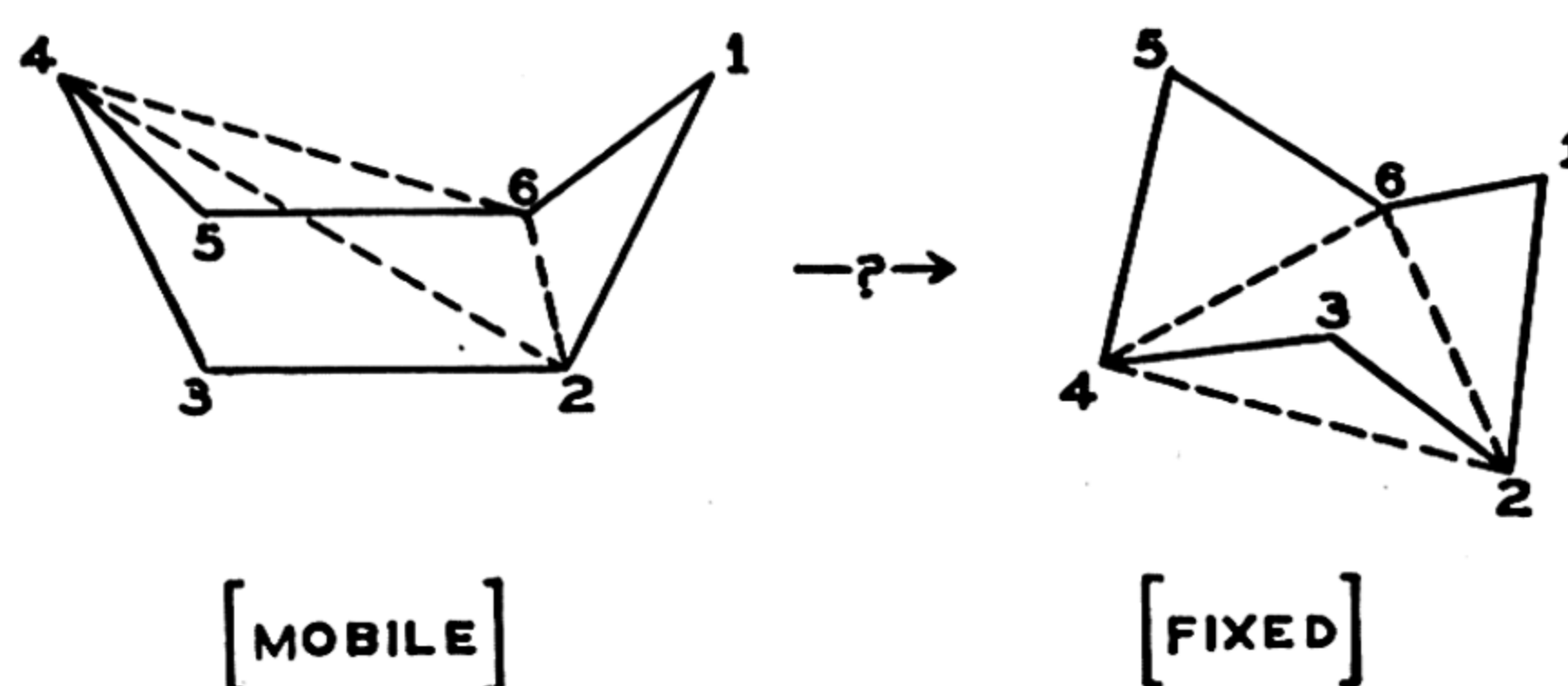
6. Isomerization by shifts of rearranged alkyl groups along the ring. The over-all changes are: (a) dehydrogenation (usually by displacement of only one hydrogen atom) plus dealkylation plus rearrangement of the alkyl; and (b) subsequent alkylation plus hydrogenation. These changes result in an exchange in position of hydrogen and new alkyl. This isomerization has not been observed in the cyclanes to date; it is a predictable combination of types 3 and 5.



7. *Cis-trans* or geometrical isomerization, *e.g.*,



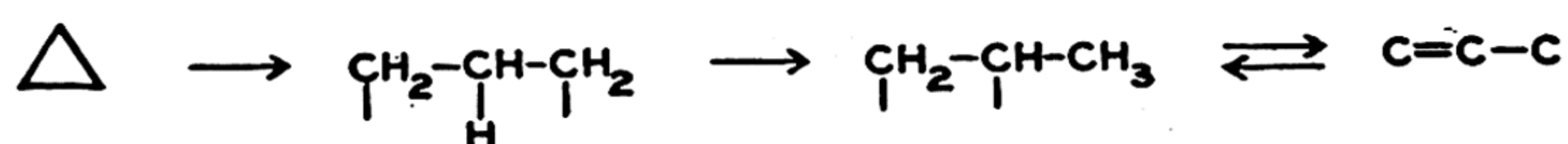
8. Multiplanar isomerization, illustrated by the multiplanar forms of cyclohexane,



These reaction directions are merely illustrations of some of the types of isomerization that may be encountered among the cyclanes and their saturated homologs. Various combinations of directions are obviously possible.

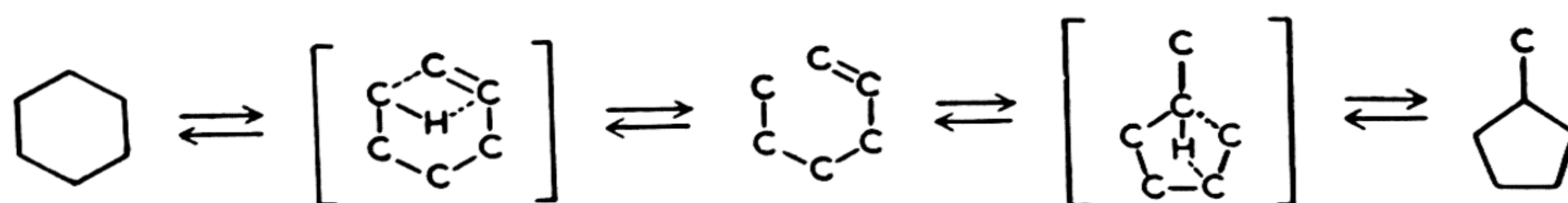
An isomerization of type 1 converts the monocyclic hydrocarbons into reactive alkenes. That of type 2 transforms certain rings into cyclohexanes, which in turn can be dehydrogenated to valuable aromatics. Types 3 and 4 are encountered often in synthetic organic chemistry, whereas types 7 and 8 are principally of theoretical interest. The first four of the 8 possible types have been observed experimentally and are well established.

Concerning the mechanism of these reactions, it should be noted that the first-two types of isomerization require ring rupture and shift of a hydrogen atom. Nef³⁹⁶ formulated the isomerization of cyclopropane as follows:



The formation of an "active trimethylene particle" and a scission of hydrogen from its central carbon atom were the essential changes elaborated upon for the isomerization. Schools of organic chemistry today emphasize the dependence of isomerizations on electronic transfer within the molecule,⁶⁴¹ rather than upon the formation of "active particles."

The role of catalyst may be that of a hydrogen carrier rather than an agent splitting C—C bonds. It should be recalled at this point that *dehydrogenating* catalysts were considered of especial importance in a mechanism of alkane isomerization involving hydrogen disproportionation. The actual C—C break within a ring may be a process proceeding through an intermediate active alkene, *e.g.*:

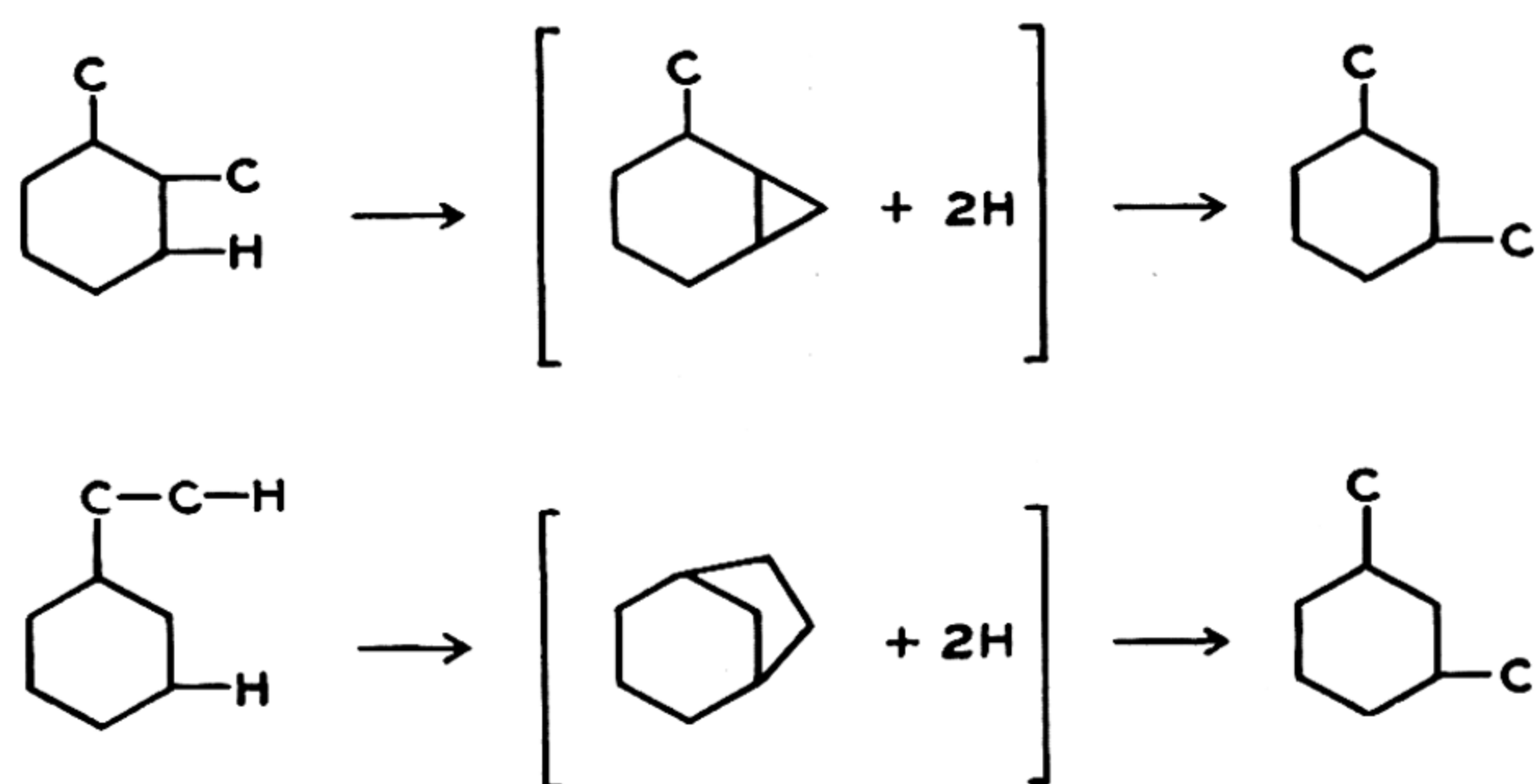


In isomerization type 2 (*i.e.*, change of ring size), still another mechanism may be considered, namely, dehydrogenation plus cyclization and successive decyclization plus hydrogenation:



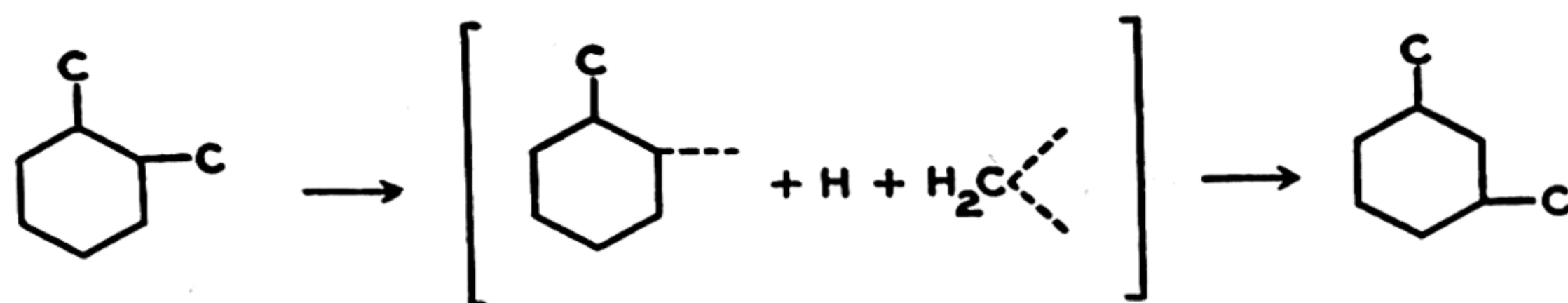
This mechanism was suggested for an acetylation reaction using cyclohexane⁶⁰² and for an isomerization of the same hydrocarbon.⁶⁷⁵ Such inter- and intramolecular hydrogenation plus dehydrogenations in the presence of aluminum halide catalysts have been observed in numerous cases.^{195, 280, 281, 523, 524} The free radical, cyclohexyl, may isomerize into methylcyclopentyl in the related reaction of cyclohexane with acetyl chloride and aluminum chloride.³⁹⁸ This mechanism is not in conflict with a dehydrogenation plus cyclization as followed by decyclization plus hydrogenation. It has been pointed out that like electrical charges may be responsible for ring expansions.⁴⁰⁶ The latter are attributed to like electrical charges in 2 adjacent ring-carbon atoms, especially if enhanced by similar charges in side-chains attached to each of these carbons. Unlike electrical charges in side-chains, according to this viewpoint, would favor ring contraction. As already pointed out, "cyclic intermediates" can be considered as a mobile system of diyl forms that seldom attains the bicyclic, "intermediate" state of transformation illustrated herein.

Isomerization types 3 and 4 proceed, as in the case of alkanes, by "migrations" of hydrogen atoms and alkyls. A particular but unproved mechanism would be the formation of a bicyclic intermediate. A temporary closure of side-chain upon the ring, via dehydrogenation, followed by a hydrogenation and decyclization, describes this mechanism:



A simpler isomerization via alkylidene groups (such as methylene), or via an alkene of alkylation, is conceivable upon admission of dehydro-

genation and decyclization ("the C—C break") as parts of the isomerization mechanism:



Isomerization types 5 and 6, with rearrangement of the side-chain itself, are not encountered because of a distribution of small new radicals along the ring (type 4). Isomerization type 7 (*cis-trans*) among the cyclanes has remained almost unobserved to date, although it is recognized that cyclic structures restrict the freedom of rotation of alkyl groups about the carbon atoms of rings.²¹³ Type 8, involving non-planar rings, will be considered in the isomerization of cyclohexanes.

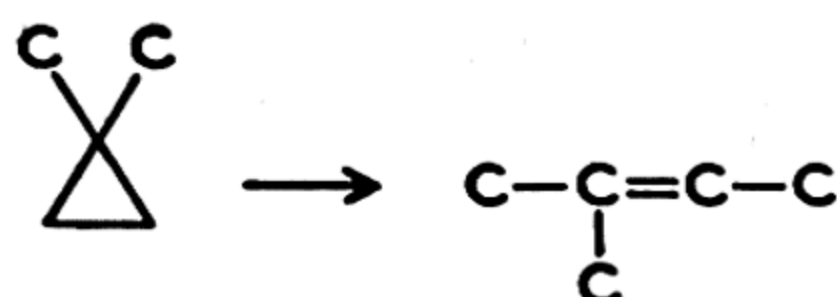
Isomerizations

Cyclopropanes. The isomerization of cyclopropane into propene, in contrast with the opposite reaction, is one of the easy isomerizations in hydrocarbon chemistry. Passage of cyclopropane through a glowing glass tube gave propene.⁵⁷⁶ While only 1-2 per cent of propene is formed at 370° in the absence of a catalyst and with long contact time,²⁷⁹ the reaction can be almost complete at 550°⁶² or 600°.⁵⁹⁰ Tubes of quartz are preferable to those of glazed or unglazed porcelain, since the former reduce polymerization.⁵⁹⁰

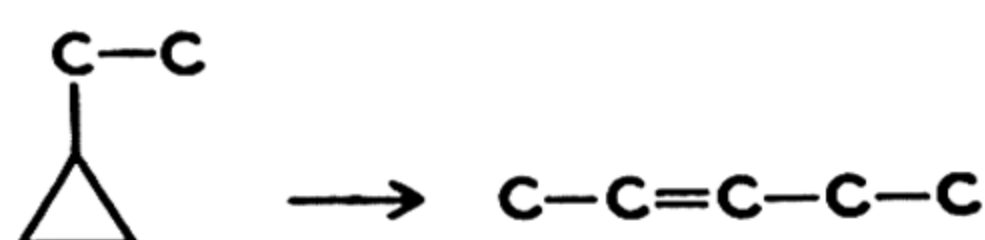
A kinetic study¹⁰⁴ of the reaction at 500° showed that the isomerization of cyclopropane is unimolecular, with an activation energy of 65.0 kilocalories per gram-mole. The propene yield was 25-65 per cent. The reaction-velocity constants are in agreement with a rate-determining step consisting of a hydrogen migration.⁴⁶⁵ Earlier workers⁵⁹⁰ found 63.9 kilocalories per gram-mole for the heat of activation at 550-650°, and pointed out that the isomerization of cyclopropane is the first example of a monomolecular reaction among gases. From heat of combustion data for propene⁴⁷⁶ and cyclopropane,²²⁴ it can be demonstrated that the exothermic heat of isomerization of cyclopropane into propene, at 25° and one atmosphere pressure, is about 4.8 kilocalories per gram-mole. This large energy liberation is due to the highly-strained condition of the cyclopropane ring.

The use of catalysts greatly reduces the temperature and time required for the formation of a given percentage of propene in the final product. Thus, cyclopropane in the presence of platinum black, air, and moisture gave 19-30 per cent of propene in 5 months at room temperature.⁵⁷⁷ At

1,1-Dimethylcyclopropane formed 92 per cent of 2-methylbutene-2 (trimethylethylene) in the presence of alumina at 340-345°:²⁷⁹

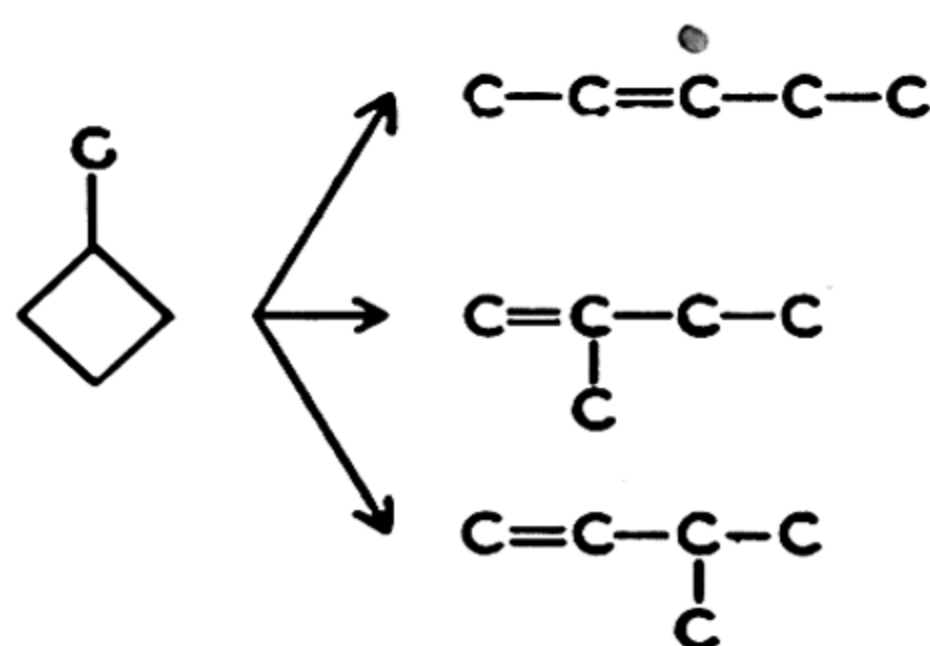


Ethylcyclopropane yielded pentene-2 when passed over alumina-asbestos at 300-310°:⁴⁷⁹



Cyclobutanes. No experimental work has been reported on the direct isomerization of cyclobutane into a butene. Thermodynamically, the reaction should proceed to a lesser extent at a given temperature than the corresponding change of cyclopropane into propene.

Methylcyclobutane isomerized over alumina at 400° into pentene-2, 2-methylbutene-1, and 3-methylbutene-1, which apparently shows that ring rupture occurs in either of the two possible places:⁴⁸⁰



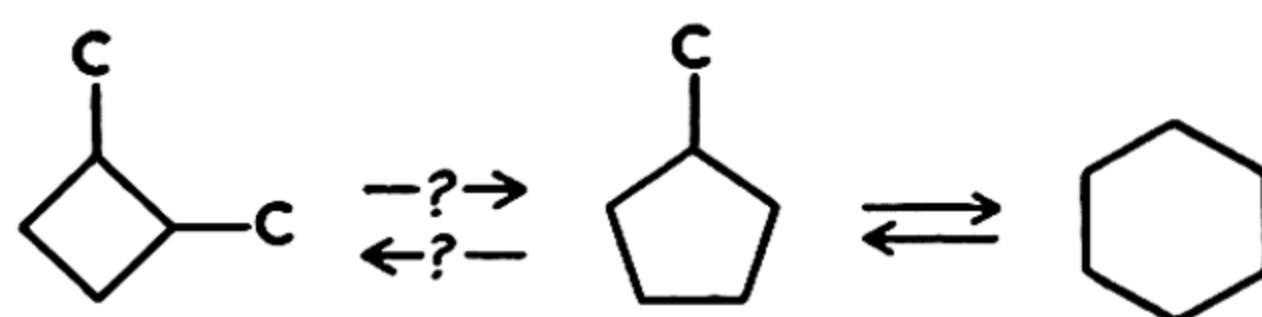
A study of the rates of formation and possible interconversion of the three resulting isomers seems desirable.

Cyclopentanes. With rings containing five or more carbon atoms, a cyclane isomerization of type 2 (change of the ring structure) takes place. However, there is some indication that an isomerization of type 1 (decyclization) also occurs.

An isomerization of cyclopentane has not been observed to date. Cyclopentane remained unchanged when heated under reflux for 8 hours with anhydrous aluminum chloride.¹²⁹

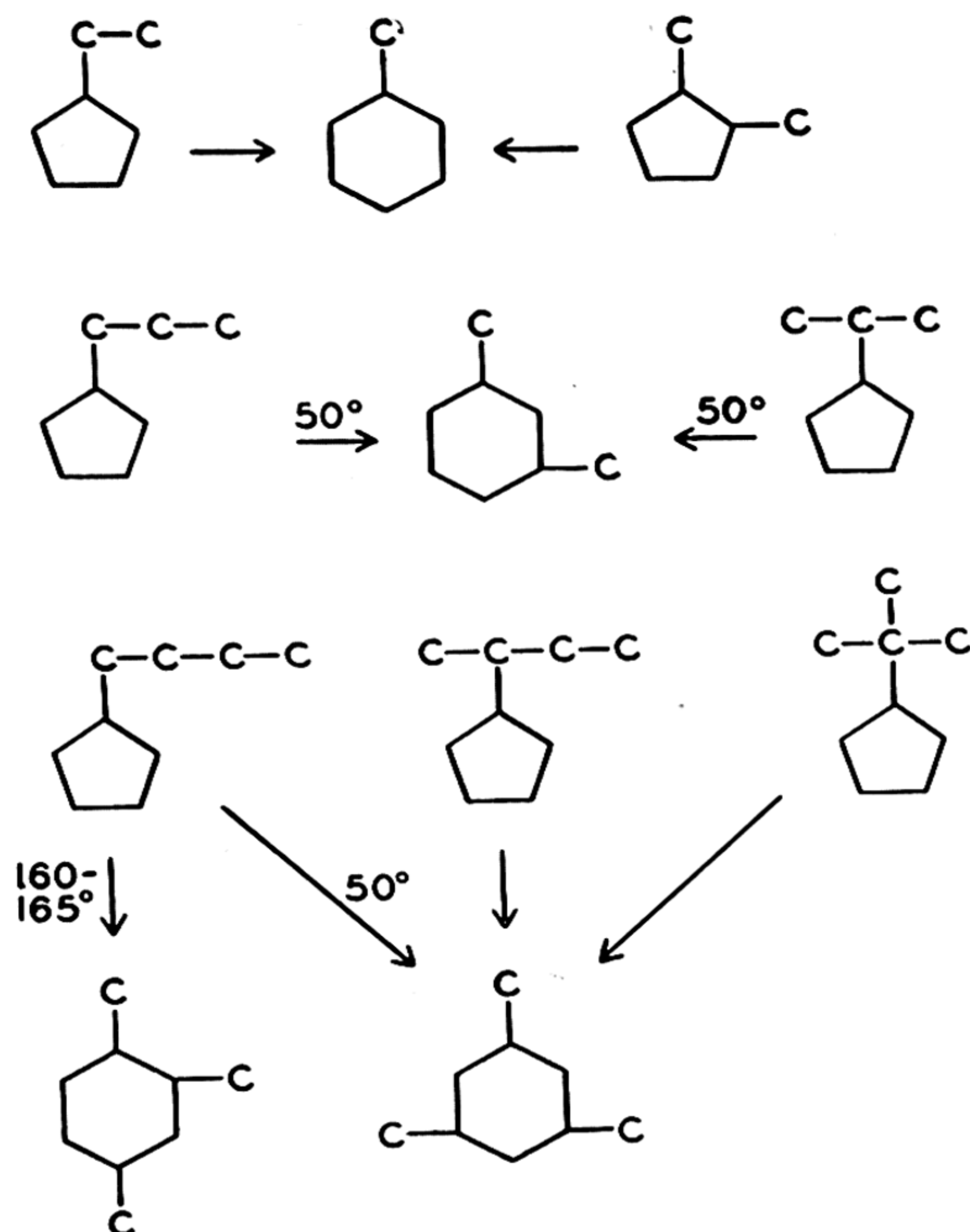
Methylcyclopentane, heated under reflux for 30 hours with aluminum chloride (30.5 per cent) plus water (0.8 per cent), underwent a reversible type 2 isomerization (change of ring size), forming an "equilibrium mix-

ture" containing 22.8 per cent of methylcyclopentane and 77.2 per cent of cyclohexane.³⁹⁹ Heated under reflux for 3 hours with aluminum chloride (20.9 per cent) and water (0.7 per cent), methylcyclopentane gave cyclohexane (58.6 per cent) and low- and high-boiling products.²¹⁵ It seems probable that methylcyclopentane when treated with a large amount of aluminum bromide gives also some 1,2-dimethylcyclobutane.⁶⁷⁵ Anhydrous aluminum chloride is reported to be also a catalyst.⁵⁹⁵ Compositions of the "equilibrium mixture" are dependent upon reaction temperatures. *Prior* to the occurrence of side reactions, these compositions at 25.1°, 61.0°, and 99.5° are respectively 12, 21.5, and 46 per cent of methylcyclopentane and 88, 78.5, and 54 per cent of cyclohexane.⁴⁴¹ "Equilibrium mixtures" prepared at 20° and 80° were found to contain respectively 11.0 and 23.4 per cent of methylcyclopentane and 88.0 and 76.6 per cent of cyclohexane.^{529a} Methylcyclopentane, heated at 500° with sulfur compounds of cobalt and of molybdenum under 100 atmospheres' initial hydrogen pressure, formed a small amount of cyclohexane:⁴⁵²



Recent work on the isomerization of alkylcyclopentanes reports yields of over 80 per cent of isomeric cyclohexanes (when the former are heated for 18 hours at 50° with 13 mole per cent of aluminum chloride and a trace of water).⁴⁴⁰ In this work, ethylcyclopentane gave methylcyclohexane; propyl and isopropyl cyclopentanes formed 1,3-dimethylcyclohexane, whereas *n*-, *sec*-, and *tert*-butyl cyclopentanes gave 1,3,5-trimethylcyclohexane. Side reactions were reported absent. However, treatment of propylcyclopentane with aluminum chloride at the elevated temperature of 140-145° gave 1,3- and 1,4-dimethylcyclohexanes and alkanes.⁵⁹⁸ Ethylcyclopentane yielded 83.4 per cent of methylcyclohexane, along with 2.6 per cent of unchanged hydrocarbon, when treated 20 hours at 110-115° with aluminum chloride.⁵⁹⁷ Isopropylcyclopentane yielded about 70 per cent of 1,3- and 1,4-dimethylcyclohexanes, along with 17 per cent of alkanes and substituted cyclopentanes, in an isomerization effected by aluminum chloride at 125-130°. ^{598a} *n*-Butylcyclopentane formed a considerable amount of 1,2,4-trimethylcyclohexane and 5.7 per cent of alkanes, upon treatment for 20-24 hours at 160-165° with aluminum chloride.⁵⁹⁶ *n*-Amylcyclopentane yielded 55 per cent of "inseparable" cyclohexane derivatives, probably tetramethylcyclohexanes, and some low-boiling and high-boiling hydrocarbons when subjected to the action of aluminum chloride at 150-155° for 20 hours.^{598b}

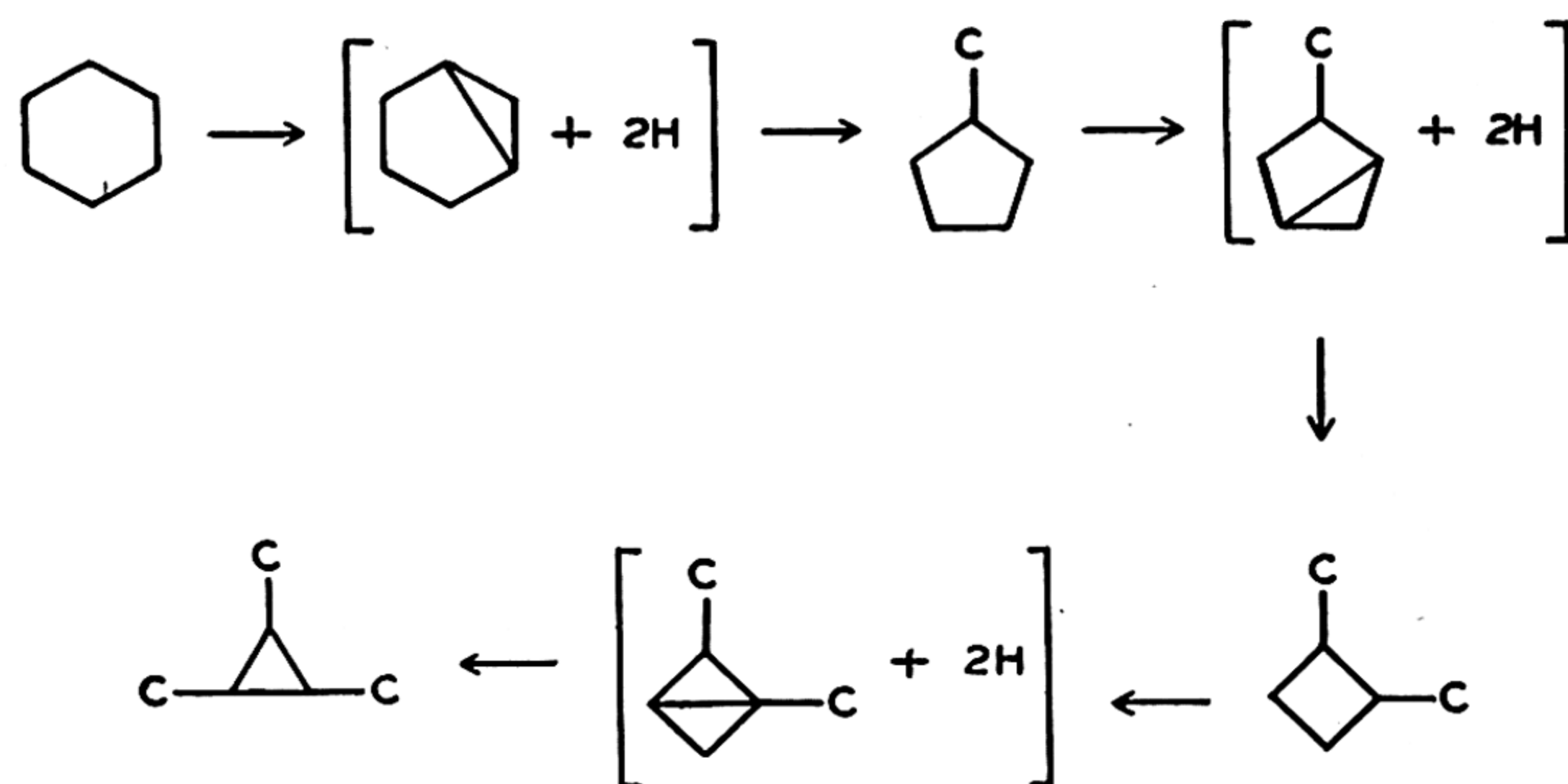
1,2-Dimethylcyclopentane was isomerized to 96.7 per cent of methylcyclohexane in the presence of aluminum chloride at 100-104°. ^{598c}



Cyclohexanes. The partial isomerization of cyclohexane to methylcyclopentane, which is a reaction with an interesting history, was first observed in 1902. When cyclohexane was heated at 330° in a potash-glass tube, the reaction was catalytic; a soda-glass tube gave negative results.¹⁶ Cyclohexane, treated with aluminum chloride for 48 hours at room temperature and afterwards heated to the boiling point, formed hydrogen chloride gas, some methylcyclopentane, and a large amount of resins.¹⁶ Considerable cyclohexane was also recovered.

In later work (1911), cyclohexane was heated with alumina (6.98 per cent) for 4 hours at 500-510° and 110-120 atmospheres' pressure, forming a small amount of methylcyclopentane, besides hydrogen, methane, and other hydrocarbons.²⁷⁵ In 1927, cyclohexane, when heated 3 days at 420° in an alkali-glass tube, gave 5 per cent of methylcyclopentane.⁵⁴⁷ Cyclohexane was treated (1929) with aluminum bromide (25 mole per cent) for 12 hours at 180°; this resulted in only a slight change.⁶⁷⁴ Later work ⁶⁷⁵ showed that cyclohexane when heated for 24 hours on a water bath with aluminum bromide (51.4 per cent) forms two fractions. One of these with b.p. of 78-80° was taken to be a "stable form" of cyclohexane, whereas the other (3.57 per cent) was stated to be dimethylcyclo-

butane. It was also claimed that aluminum chloride gives about the same results as aluminum bromide. The last catalyst was considered to catalyze the following sequence of reactions:



Apparently the action of aluminum bromide does not stop with the formation of methylcyclopentane, but goes on to form dimethylcyclobutane, trimethylcyclopropane, and probably alkanes.⁶⁷⁵

Cyclohexane, in 1933, was heated under reflux for 3 hours with aluminum chloride (29.8 per cent) plus water (0.8 per cent), giving methylcyclopentane (5 per cent), unaltered cyclohexane, and probably some *n*-hexane.³⁹⁹ Dimethylcyclobutane was not obtained as a product, and the reported equilibrium mixture for the reflux temperature consisted of methylcyclopentane (22.8 per cent) and cyclohexane (77.2 per cent). In the following year, an investigation²⁸⁰ was carried out with cyclohexane and aluminum chloride (9.77 per cent) in the presence of hydrogen chloride for 24 hours at 150°. The reaction products were hydrogen, isobutane (1327 cc. per 307.4 g. cyclohexane), methylcyclopentane, some unchanged cyclohexane, 1,3-dimethylcyclohexane (6.5 per cent), dimethyldicyclopentyl (9 per cent), and dicyclohexyl (3 per cent). The combined mixture of methylcyclopentane and unchanged cyclohexane accounted for only 60 per cent of the original cyclohexane. A yield of 16.0 per cent of methylcyclopentane was obtained in the treatment of cyclohexane with aluminum chloride and some water.²¹⁵ The experimental conditions were incompletely disclosed, but the products also included isohexanes, 1,3-dimethylcyclohexane, dimethyldicyclopentyl, dicyclohexyl, and some unreacted cyclohexane. These side products are some of those reported previously.²⁸⁰ The composition of the "equilibrium mixture" or distillate is highly dependent upon temperature. The "equilibrium amount" of methylcyclopentane steadily increases with any rise in reaction temperature until, at 140°, it reaches that of the cyclohexane.^{529a} The compositions for equilibrium conditions at 25.1°, 61.0°, and 99.5°,

in the presence of either partially hydrated aluminum chloride or aluminum bromide with hydrogen bromide, were mentioned in the discussions on methylcyclopentane.⁴⁴¹

The isomerization of cyclohexane into methylcyclopentane is an interesting reaction from the thermodynamic standpoint, since energy must be added or absorbed from the surroundings of the molecules. The endothermic heat of isomerization of cyclohexane into methylcyclopentane is 3.83, or 7.30 kilocalories per gram-mole (for the temperature ranges 25.1°-61° and 61°-99.5°, respectively.⁴⁴¹ Other values for the heat of isomerization of cyclohexane into methylcyclopentane are 3.51 and 3.93 kilocalories per gram-mole at 25°, obtained respectively from equilibrium measurements²¹⁵ and from new values of the heats of combustion of these hydrocarbons.³⁸⁶ The corresponding free energy changes are 1.15 kilocalories²¹⁵ and 0.95 kilocalories³⁸⁶ per gram-mole.

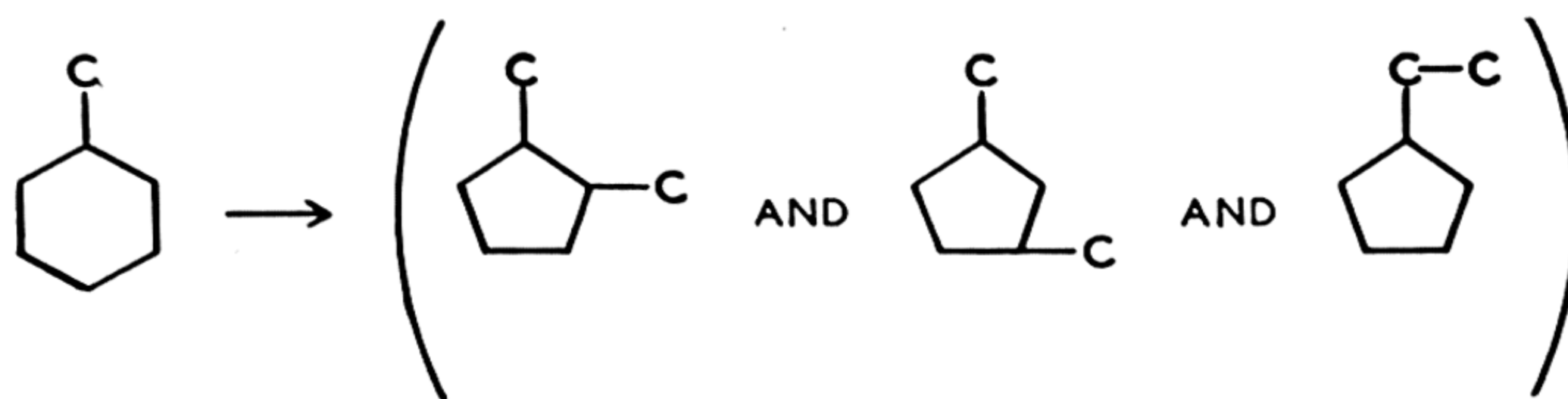
Recent work has demonstrated that the yield of methylcyclopentane can be increased by use of other catalysts. Cyclohexane heated at 400° under 140-350 atmospheres' pressure of hydrogen in the presence of molybdenum disulfide (MoS₂) gave a considerable amount of methylcyclopentane (62 per cent of the *recovered* hydrocarbons), together with *n*-hexane and isohexanes.⁴⁵⁴ Gases, unsaturated hydrocarbons, and aromatics developed as additional products at 500°. ^{453b} A practically complete isomerization of cyclohexane into methylcyclopentane occurred in one hour at 500° under 100 atmospheres' initial pressure of hydrogen in the presence of sulfur compounds of cobalt and of molybdenum.⁴⁵² Cyclohexane formed 67.7 per cent of methylcyclopentane, together with 0.6 per cent of aromatics, when passed at 411° and 200 atmospheres' hydrogen pressure over Japanese acid clay supporting molybdenum sulfide.⁴ A mechanical mixture of molybdenum trioxide and sulfur proved less active as a catalyst, resulting in only 10.9 per cent of methylcyclopentane at 439° and 262 atmospheres' hydrogen pressure.⁵ The yield was increased to 15.3 per cent by simultaneously halving the time of treatment and slightly lowering the reaction temperature and pressure.^{5, 5a} The use of a catalyst composed of molybdenum sulfide, supported upon a Japanese acid clay that was previously activated by mineral acids, was effective in forming 17.2 per cent of methylcyclopentane under the foregoing, less-drastic, reaction conditions.^{5a}

Methylcyclohexane occurs in stable and unstable forms, which are possibly the multiplanar "C" and "Z" molecules demanded by the Mohr³⁷⁸ and Sachse⁴⁹⁸ theory. Stable methylcyclohexane (b.p. 100.4-100.7°/773 mm. Hg, $D_4^{20} = 0.7704$, $n_D^{20} = 1.42410$) was prepared by: (1) hydrogenation of certain methylcyclohexenes (via phosphorus pentoxide on 1-, 3-, or 4-methylcyclohexanols), or (2) the aging for 7 days,

or heating to 40-60°, of unstable methylcyclohexane (b.p. 100.2-100.4°/768 mm. Hg, $D_4^{20} = 0.7679$, $n_D^{20} = 1.42306$) (via hydrogenation of the methylcyclohexene from 2-methylcyclohexanol and phosphorus pentoxide).⁶¹¹ This is the first experimental evidence for an isomerization involving the multiplanar structure of the cyclohexane hydrocarbons. The validity of this work has been questioned⁶⁴⁴ and answered.⁶¹² The dehydration of 2-methylcyclohexanol and hydrogenation of methylcyclohexenes were investigated subsequently, although without definite evidence for or against multiplanar structure.⁴⁴⁶ Typical preparations of the unstable form of methylcyclohexane (b.p. 100.4°/763 mm. Hg, $D_4^{20} = 0.7678$, $n_D^{20} = 1.42306$; b.p. 100.5°/764 mm. Hg, $D_4^{20} = 0.7676$, $n_D^{20} = 1.42311$) resulted from the heating of 2- and 4-methylcyclohexanone semicarbazones with sodium ethoxide.¹²⁸ These preparations, upon standing for several days, formed stable methylcyclohexane (b.p.?, $D_4^{20} = 0.7694$, $n_D^{20} = 1.42321$; b.p. 100.4°/758 mm. Hg, $D_4^{20} = 0.7695$, $n_D^{20} = 1.42326$). According to the last experiments, the density and refractive index of the stable form are only slightly higher than that of the unstable one. Theoretically, the multiplanar "C" form should be very mobile, since a continuous series of tensionless positions is available for the molecule.¹¹¹

Methylcyclohexane, when heated with aluminum bromide, was recovered unchanged.⁶⁷⁴ The reaction conditions were not stated. Methylcyclohexane did not isomerize when treated with aluminum chloride (25 per cent) at 140-150°.⁵⁷¹ On the other hand, heating of methylcyclohexane under reflux for 10 hours with aluminum chloride (25 per cent) gave a trace of (*cis* + *trans*)-1,2-dimethylcyclopentane (0.003 per cent), 2-3 per cent of combined gases (hydrocarbons, mostly isobutane) and polymers, together with much methylcyclohexane.⁴⁰⁰ Methylcyclohexane yielded 5.4 per cent of ethylcyclopentane, along with 80.9 per cent of unchanged hydrocarbon, when treated 20 hours at 110-115° with aluminum chloride.⁵⁹⁷ Recently, methylcyclohexane was heated at 80° under pressure for 10 hours with 5 per cent each of aluminum chloride and hydrogen chloride.^{529a} This treatment resulted in the formation of about 3.5 volume-per cent of total *trans*-1,2- and *trans*-1,3-dimethylcyclopentanes, along with a little cyclohexane.

Methylcyclohexane, when reacted in the presence of molybdenum disulfide (MoS₂) for 26 hours at 400° under 350 atmospheres' pressure of hydrogen, gave 50 per cent of combined 1,2- and 1,3-dimethylcyclopentanes, together with a trace of ethylcyclopentane, and some alkanes, principally of iso- structure.⁴⁵⁵ There was no formation of 1,1-dimethylcyclopentane:



Isomerizations of types 3 and 4, involving side-chains of the cyclohexane homologs, take place in the presence of aluminum chloride. 1,1-Dimethylcyclohexane yields 1,2-, 1,3-, and 1,4-dimethylcyclohexanes when isomerized at 80° with 5 per cent of aluminum chloride and 15 per cent of hydrogen chloride under pressure.^{529a} Ortho and para dimethyl derivatives isomerize to meta compounds, but ethyl-substituted cyclohexane gives the corresponding methyl derivatives. The following set of isomerizations has been observed: ^{228, 571}

(1) 1,3-Dimethylcyclohexane from either 1,2- or 1,4-dimethylcyclohexane treated for 7 hours at $115-120^{\circ}$ with aluminum chloride (23 per cent).

(2) 1,3-Dimethylcyclohexane from ethylcyclohexane heated for 8 hours at $115-120^{\circ}$ with aluminum chloride (21 per cent).

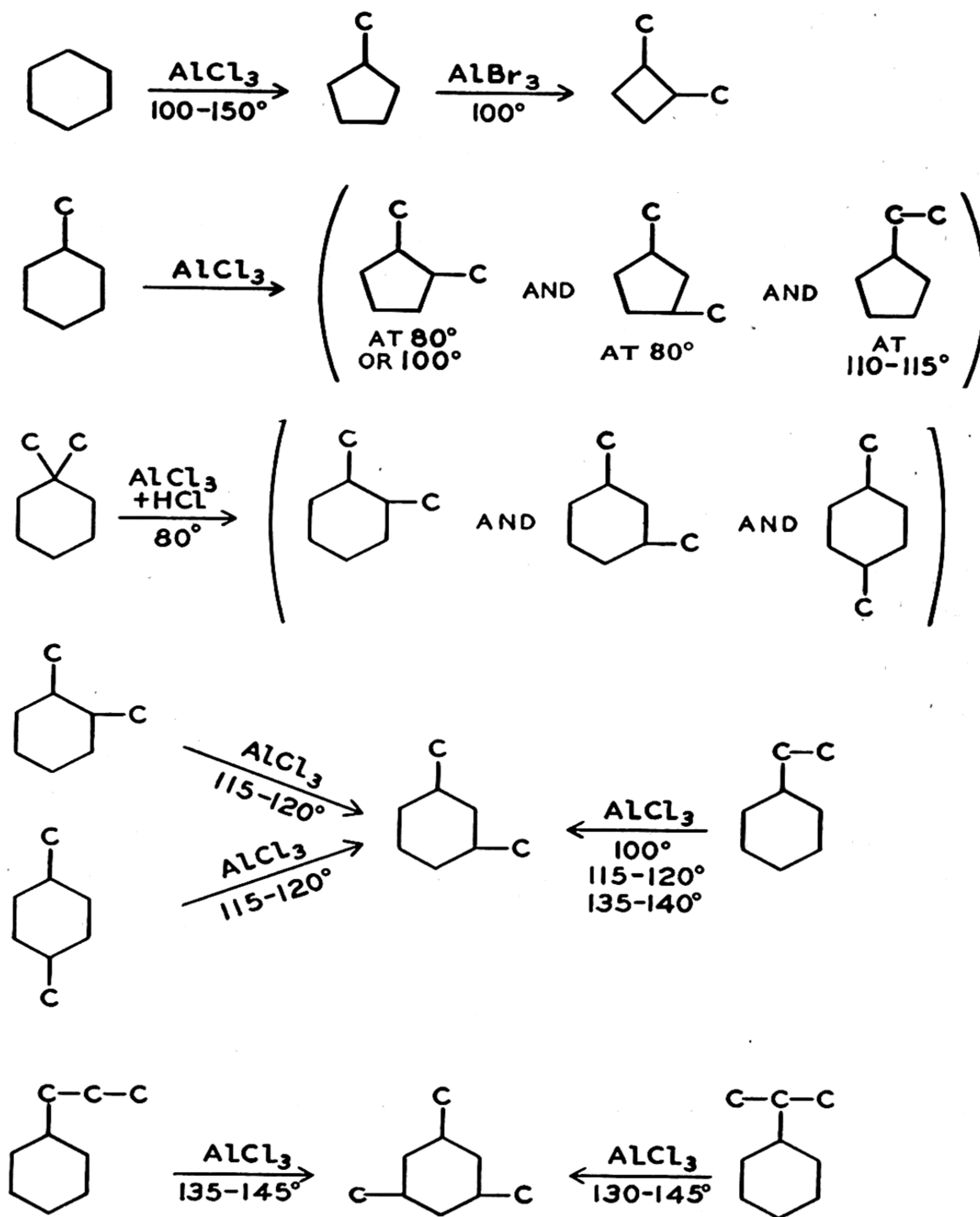
(3) Trimethylcyclohexane from *n*-propylcyclohexane treated for 7.5 hours at $135-145^{\circ}$ with 30 per cent of aluminum chloride, or from isopropylcyclohexane treated for 7 hours at $130-145^{\circ}$ with 23 per cent of the same catalyst.

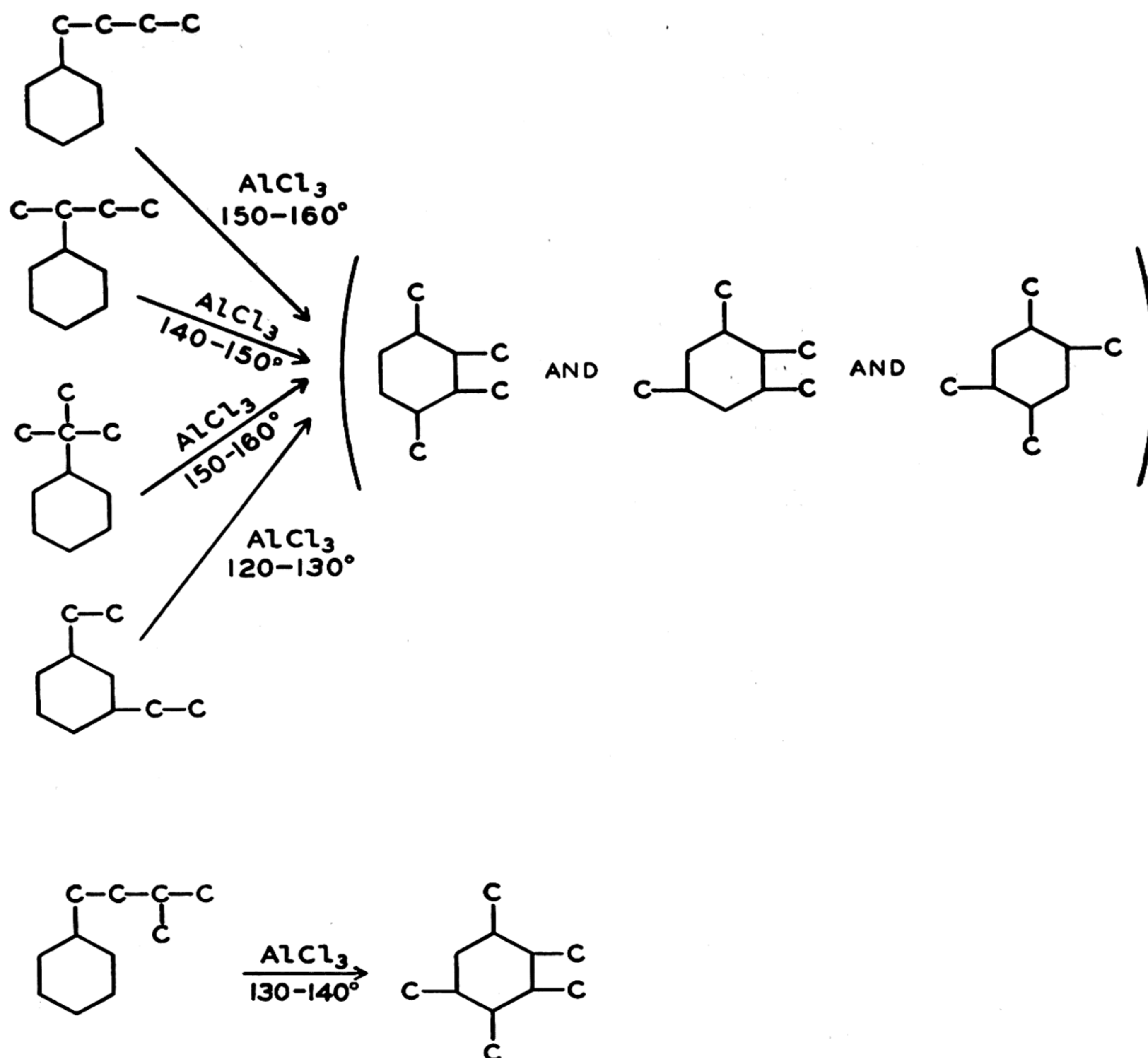
(4) Tetramethylcyclohexane from *n*-, *sec*-, or *tert*-butylcyclohexanes heated for 8 hours at $150-160^{\circ}$ with aluminum chloride (20-23 per cent).

(5) Tetramethylcyclohexane from 1,3-diethylcyclohexane treated for 4 hours at $120-130^{\circ}$ with aluminum chloride (23 per cent).

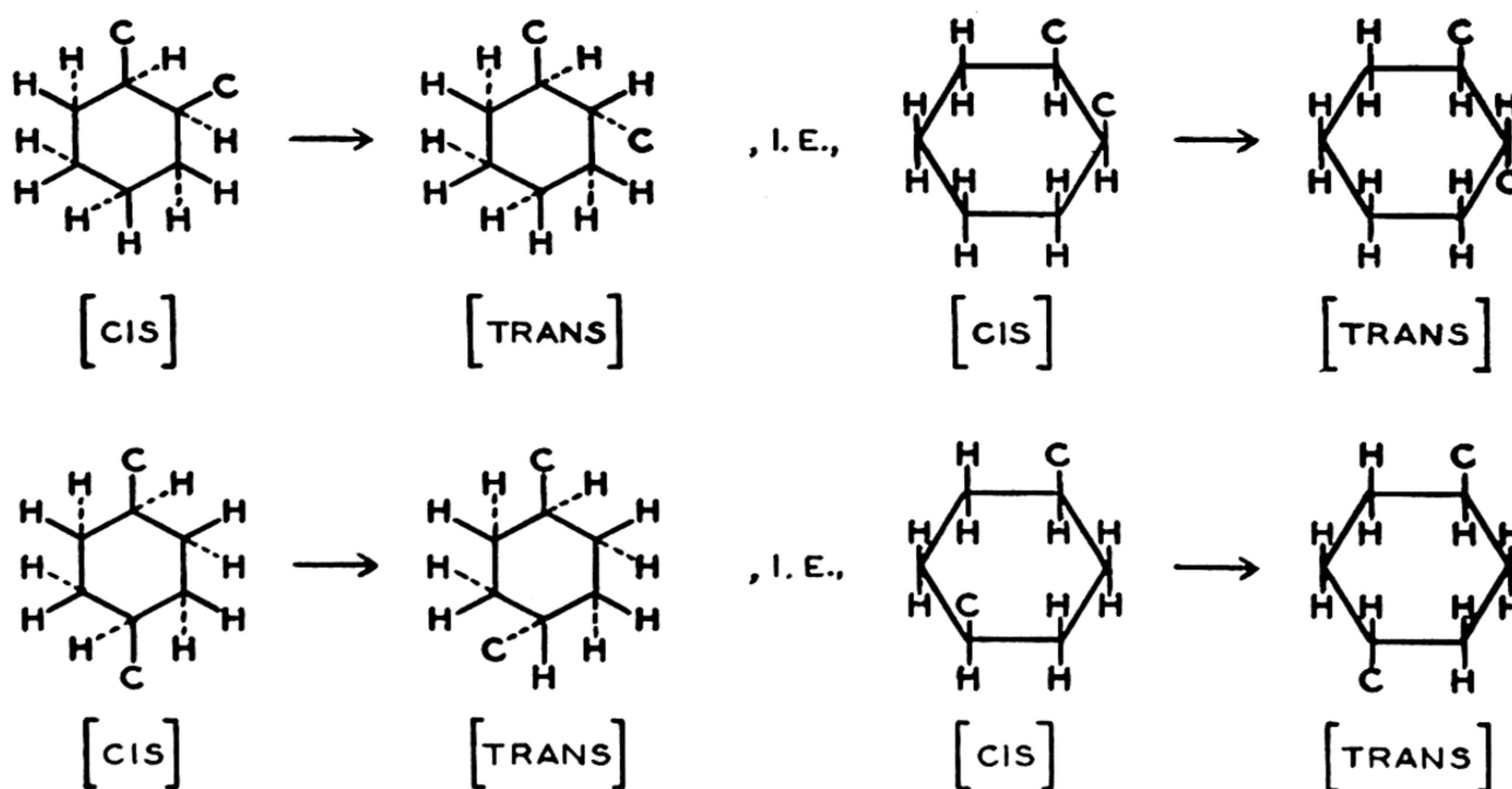
(6) Pentamethylcyclohexane, besides methylcyclohexane, tetramethylcyclohexane, *n*-butane and isobutane, from the treatment of isoamylcyclohexane for 5 hours at $130-140^{\circ}$ with aluminum chloride (17 per cent).

The formation of 1,3-dimethylcyclohexane was reported also from ethylcyclohexane and anhydrous aluminum chloride (10 per cent) at $135-140^{\circ}$.⁵⁹⁹ 1,3,5-Trimethylcyclohexane resisted the action of aluminum chloride.^{598ab} A 20 hours' treatment at $140-147^{\circ}$ yielded 3 per cent of alkanes, 9 per cent of alkylcyclopentanes (trimethylcyclohexane isomers?), and 88 per cent of unchanged initial hydrocarbon. The isomerizations of cyclohexane and its homologs occurring in the presence of aluminum halides are summarized as follows:

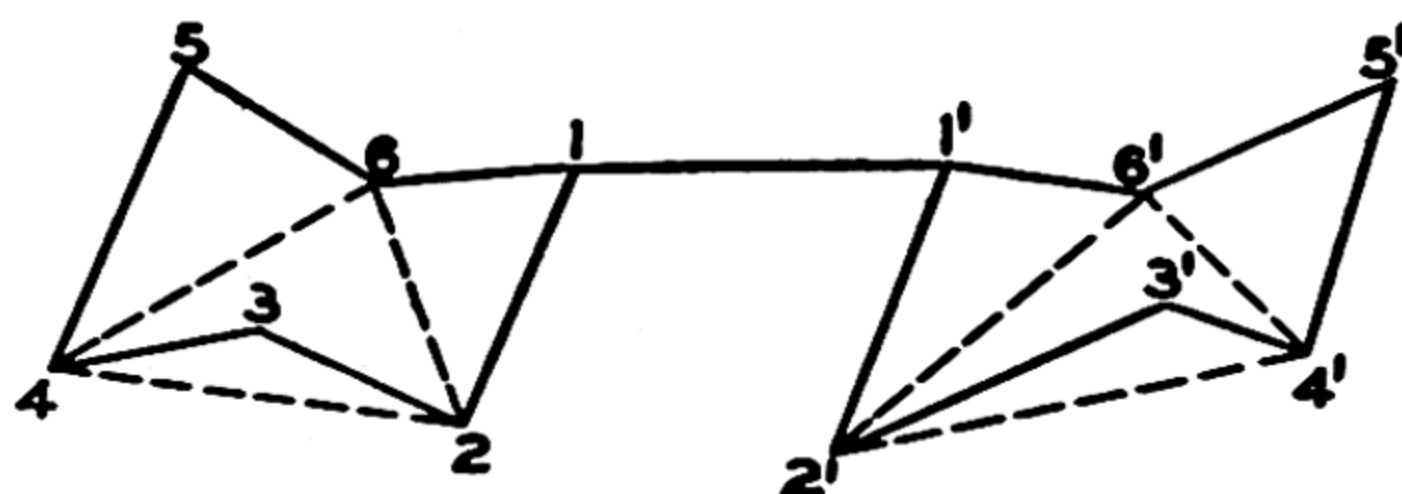




Passage of the *cis* forms of 1,2- and 1,4-dimethylcyclohexanes with hydrogen over nickel at 175° gave the *trans* forms.⁶⁷¹ The following diagrams are two of several equivalent ways of expressing these isomerizations:

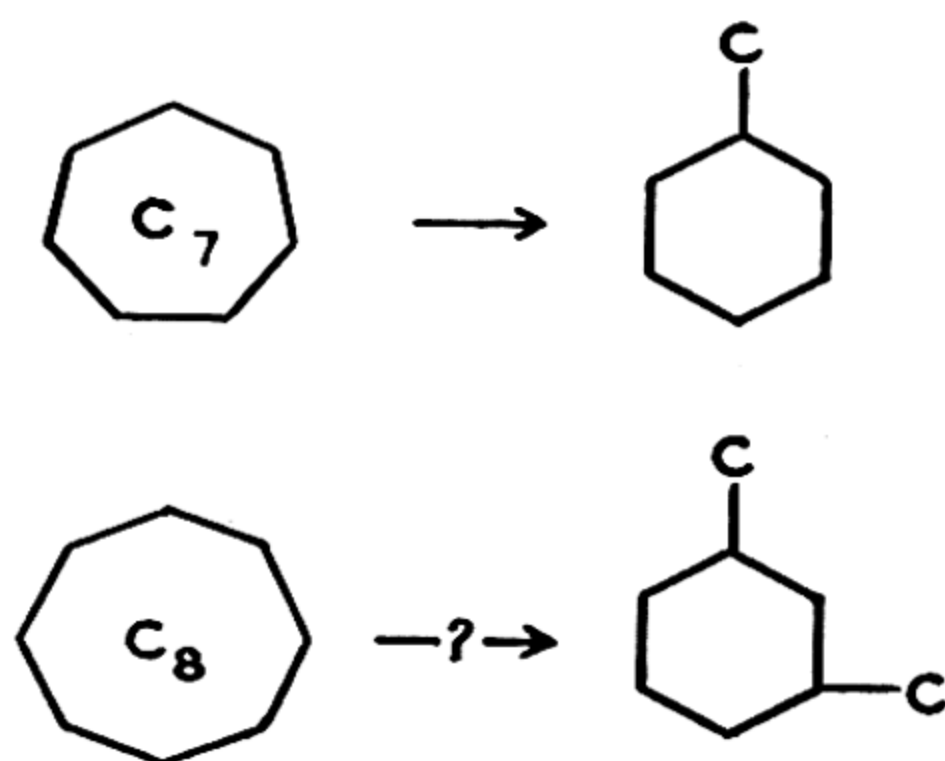


Dicyclohexyl (b.p. $234^{\circ}/750$ mm. Hg, $D_4^{20} = 0.8840$, $n_D^{20} = 1.4807$), treated for a long period with aluminum chloride at $15-20^{\circ}$ or better at 100° , was converted into an isomer of lower boiling point, density, and index of refraction (b.p. $217-219^{\circ}$, $D_4^{20} = 0.8592$, $n_D^{20} = 1.4663$), which was taken as indicative of the presence of *trans-trans*-dicyclohexyl.³⁴⁹ The product corresponds approximately to a previously described "labile" form of dicyclohexyl (b.p. $219.5-221.5^{\circ}/750$ mm. Hg, $D_4^{20} = 0.8809$, $n_D^{20} = 1.47758$).⁵²⁷ Low values of the physical constants of pure geometrical isomers are characteristic generally of stable structure and less free energy. *Trans* isomers, for example, have a higher vapor pressure at a given temperature.⁶⁸¹ Therefore, the lowered constants of the product may be indicative of two united ("chair") forms of cyclohexyl:

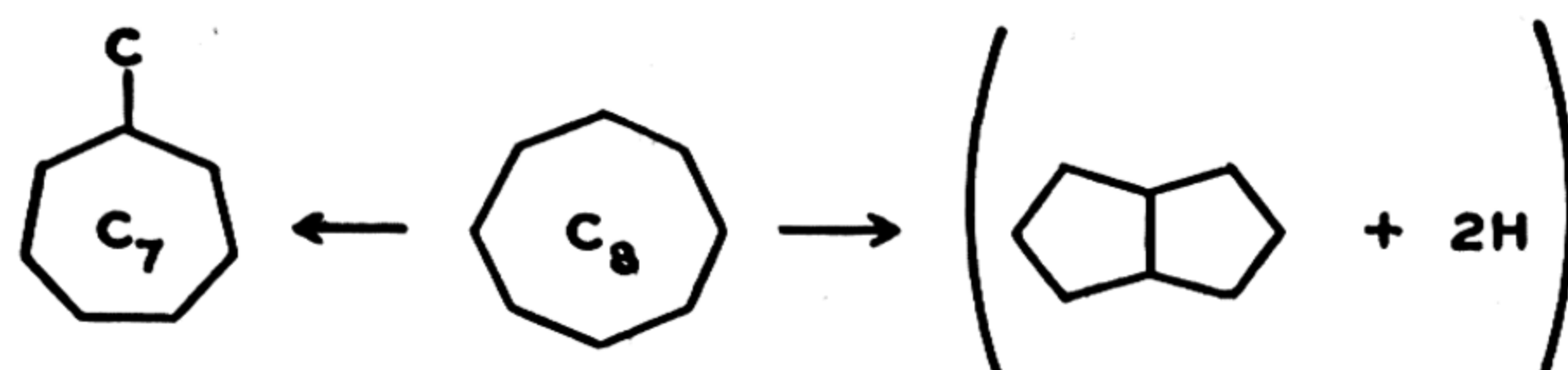


Other possibilities include the presence of methylcyclopentylcyclohexyl and/or dimethyldicyclopentyl.

Cycloheptane and Larger Cyclanes. Cycloheptane at 235° and cyclooctane at $205-210^{\circ}$ isomerized to methylcyclohexane and dimethylcyclohexane, respectively, when passed as vapors over a nickel catalyst in the presence of hydrogen.⁶⁵⁰ Higher temperatures caused a dehydrogenation to aromatics; ⁶⁵⁰ cycloheptane was converted partially into toluene by means of platinized charcoal and hydrogen at $300-340^{\circ}$.⁵⁹⁴ Cycloheptane yielded 97-98 per cent of methylcyclohexane when treated with aluminum chloride at $117-125^{\circ}$ for 20 hours.^{598aa} The foregoing isomerizations are non-reversible reactions:



Platinum catalyzed the isomerization of cyclooctane into methylcycloheptane at 300° .⁶⁶⁷ This product was accompanied by an equal amount of bicyclo[3.3.0]octane.



Cyclopentadecane and cycloheptadecane remained unchanged when heated with hydrogen iodide, indicating considerable ring stability.⁴⁸⁵

The isomerizations of cyclanes and cyclanes with saturated side-chains are given in Table 17, p. 290.

Conclusions

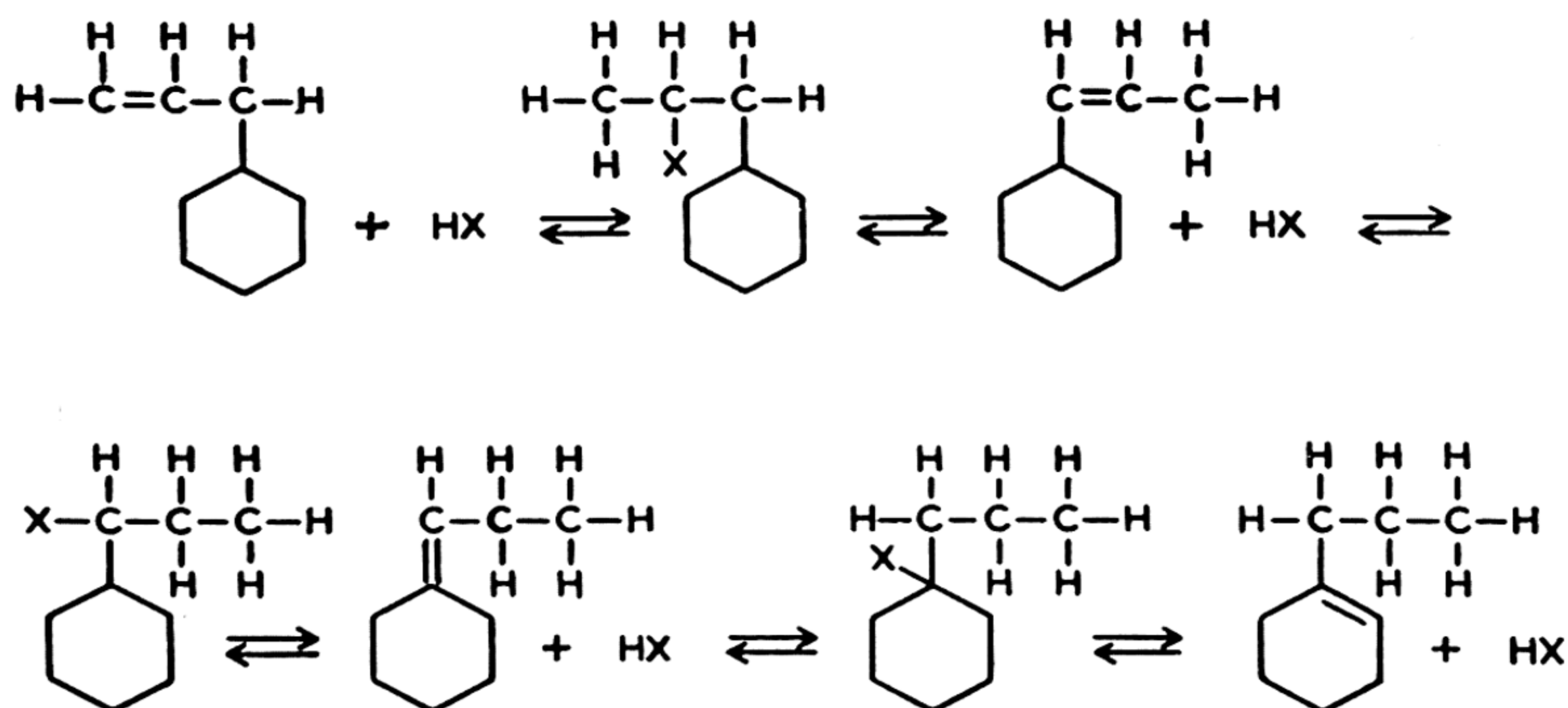
1. Cyclanes and their alkyl derivatives isomerize by changing into: alkenes, cyclanes of smaller ring size (with increased number of side-chains), cyclanes of same ring size (with altered side-chains or side-chains distributed about the ring as methyl groups), or cyclanes of increased ring size at the expense of a side-chain.

2. Cyclohexanes of unstable geometrical and multiplanar structures can be expected to isomerize into the corresponding stable form.

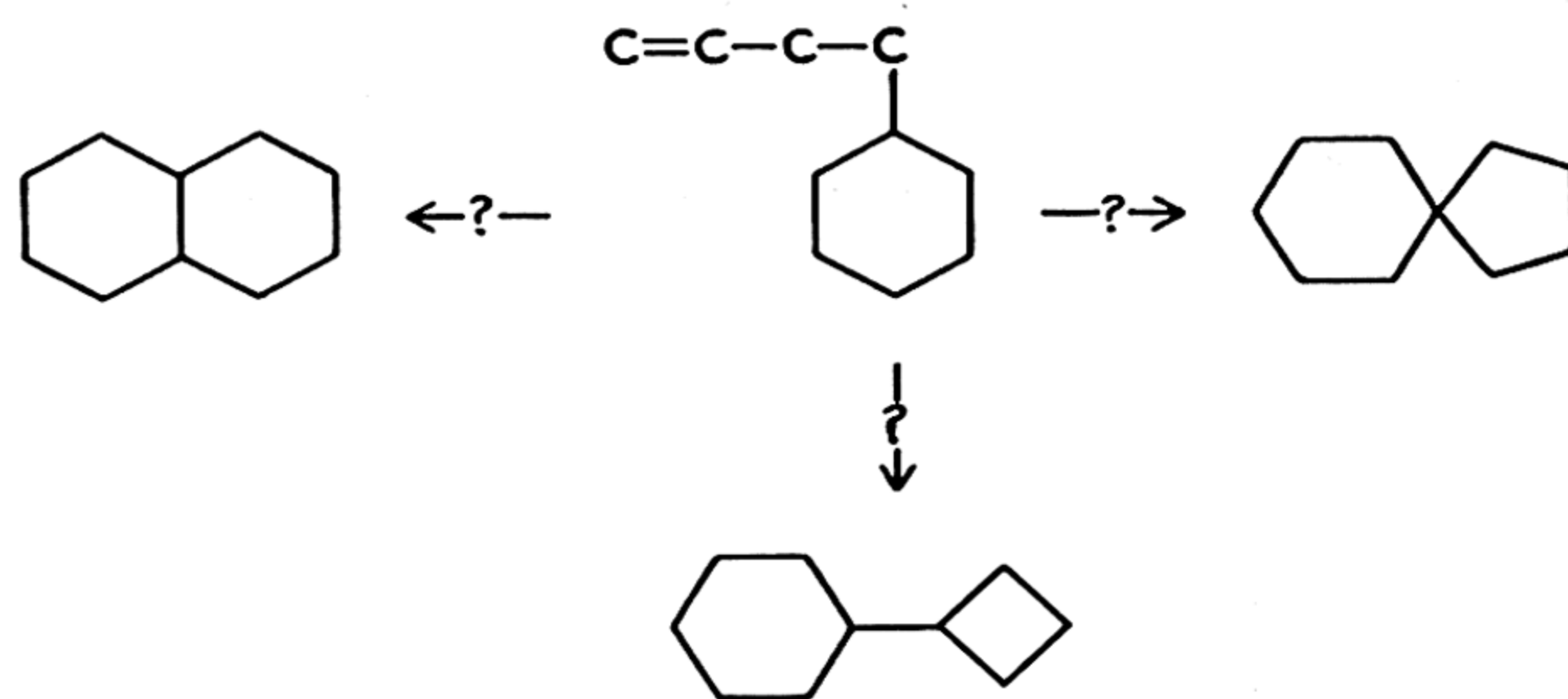
CYCLANES WITH UNSATURATED SIDE-CHAINS

Mechanism

Cyclanes containing unsaturated side-chains are noted for their formation of cyclenes and alkadienes. The simplest isomerization observable consists of a change in the location of an unsaturated bond in the side-chain. The mechanism involved may be dehydrogenation plus cyclization, followed by decyclization plus hydrogenation. Addition-product formation and subsequent regeneration of the catalyst would account also for the reactions. With acid catalysts, in particular, a shift of the double bond into the ring may occur:



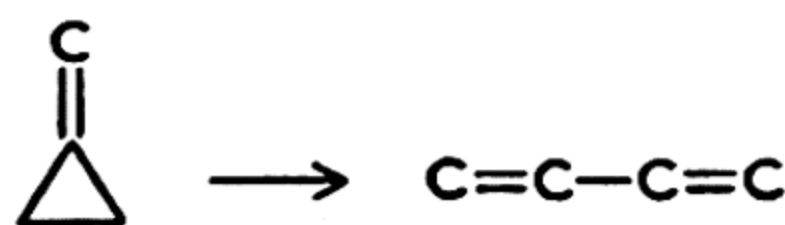
An isomerization of a cyclane with an unsaturated side-chain into a dicyclyl or into a bicyclane has not been reported to date. Isomerization should lead also to the spiranes, provided that the condition of strain does not decrease greatly the stability of the resulting isomer and, further, that the proper catalyst or reaction conditions can be found:



The reported isomerizations of cyclanes with an unsaturated side-chain into alkadienes can be considered as reactions resulting from ring instability (at temperature points where conjugated alkadienes are relatively stable).

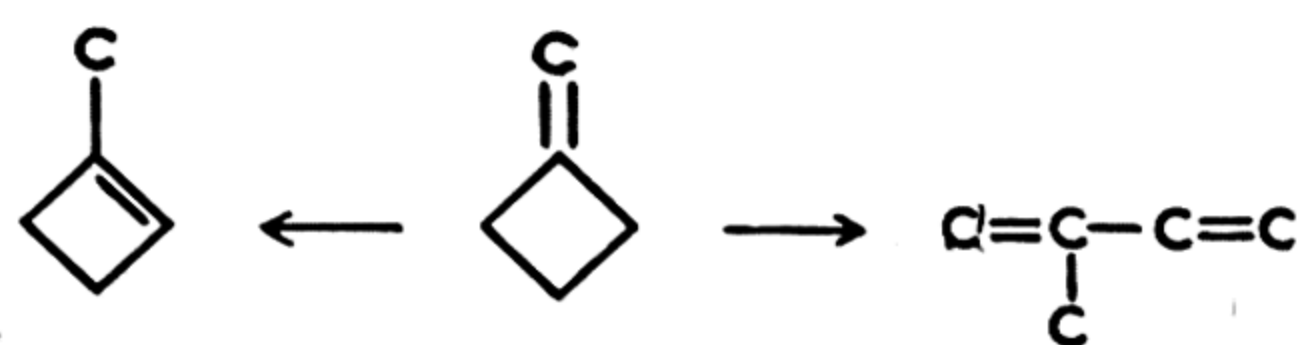
Isomerizations

Cyclopropanes. Methylene cyclopropane isomerized to butadiene-1,3 in the presence of alumina at 350°; ³⁷²

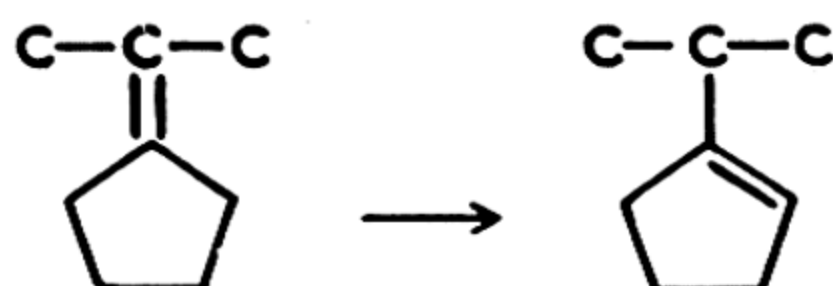


Vinylcyclopropane, although it has been prepared,¹³⁴ has not been studied from the standpoint of isomerization. Earlier preparations,^{237, 289} taken to be vinylcyclopropane and upon which studies of isomerization were conducted, were shown by a later investigator¹⁸⁸ to consist essentially of methylenecyclobutane with some 1-methylcyclobutene-1. "Spirocyclane"⁶⁷² is the same mixture taken to be spiropentane.

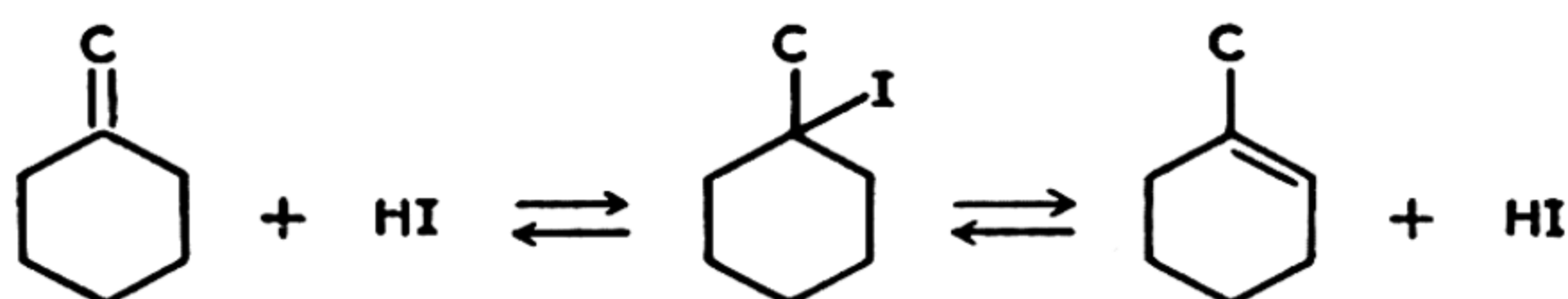
Cyclobutanes. Methylene cyclobutane isomerized to 1-methylcyclobutene-1 with alumina at 300°,^{187, 189, 289} sodium at 180-185°,⁶⁷² or when heated with zinc bromide plus basic zinc bromide and dilute alcohol.¹⁸⁹ Alkalies, sulfuric acid, or traces of hydrogen bromide were effective also.²³⁸ Formation of 2-methylbutadiene-1,3 (isoprene) and *p*-cymene occurred over alumina at the more elevated temperature of 395-430°.¹⁴⁰ Some pentene-2 is formed also;¹⁴⁰ this is indicative of a hydrogenation-scission of 1-methylcyclobutene-1.



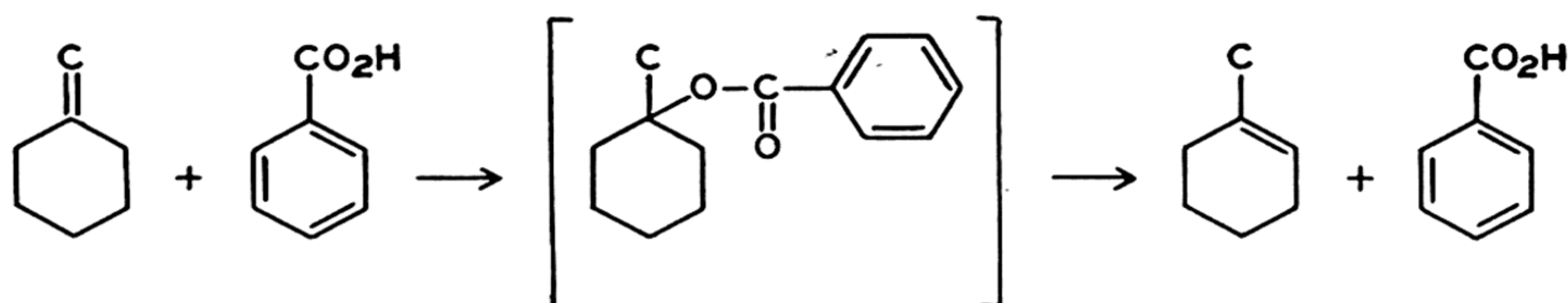
Cyclopentanes. Isopropylidenecyclopentane when heated 10 hours with alcoholic sulfuric acid gave 1-isopropylcyclopentene-1: ⁶³⁰



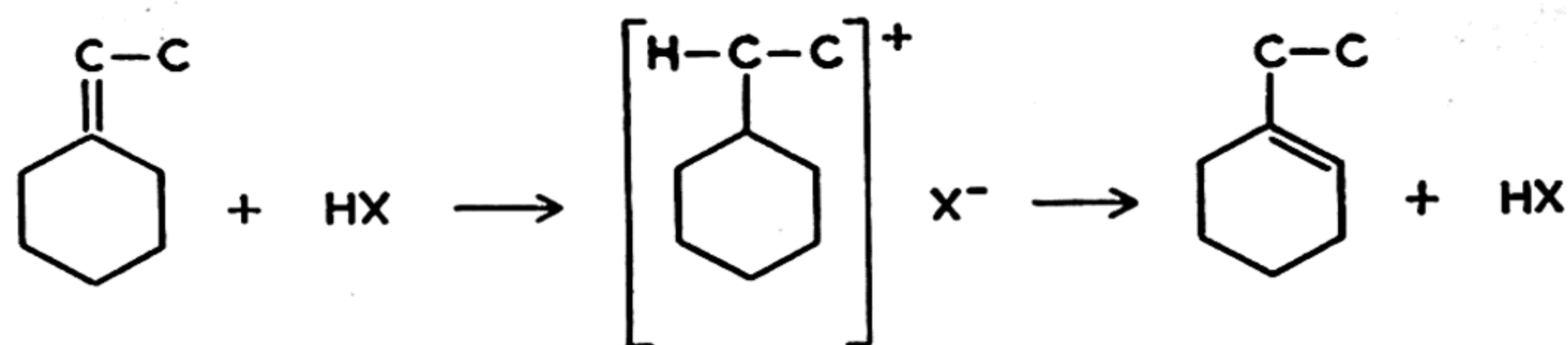
Cyclohexanes. Methylene-cyclohexane isomerized partly to 1-methylcyclohexene-1 under the action of quinoline hydriodide plus quinoline, for 3 hours at 140°, or of benzoic acid for 7 hours at 170.¹⁸¹ Quinoline alone is ineffective at the boiling point (145°) of the mixture, but quinoline hydriodide with an excess of quinoline is very effective when heated under reflux. The mechanism of isomerization was given as follows:



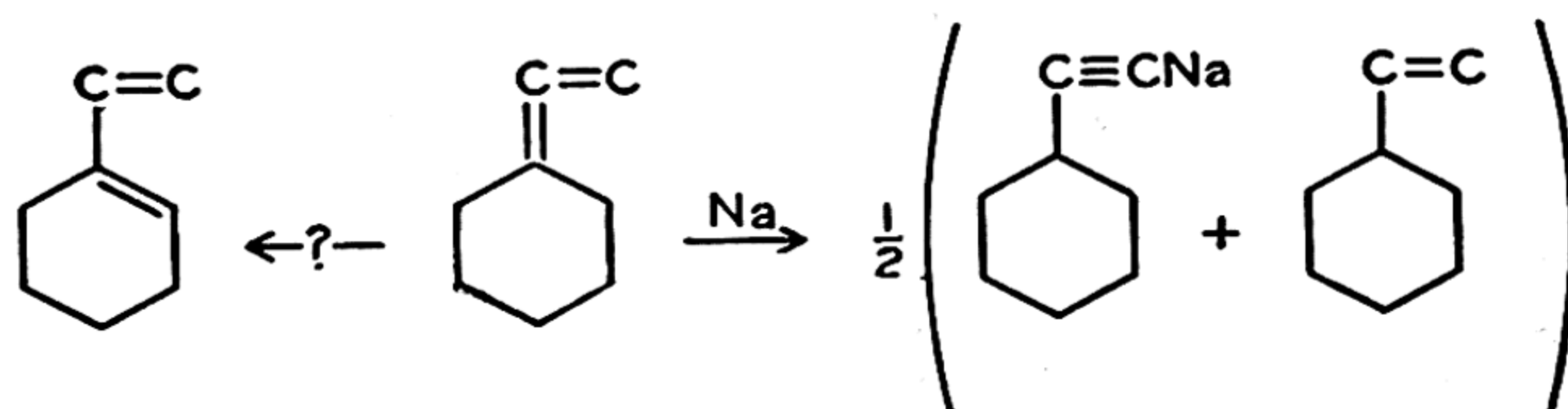
The requisite free hydrogen iodide was believed to result from thermal instability of quinoline hydriodide. The isomerization is reversible; alcoholic potash at 170° had no effect upon methylenecyclohexane.¹⁸¹ Previous workers,⁶⁶⁸ investigating the same reaction with quinoline hydriodide, considered it to be an isomerization of bicyclo[3.1.1]heptane ("1,3-methylenecyclohexane") into 1-methylcyclohexene-1. Methylene-cyclohexane, when boiled with alcoholic sulfuric acid, also gives 1-methylcyclohexene-1.⁶²³ The following mechanism describes the isomerization using benzoic acid (based upon the analogous hydrogen iodide example):



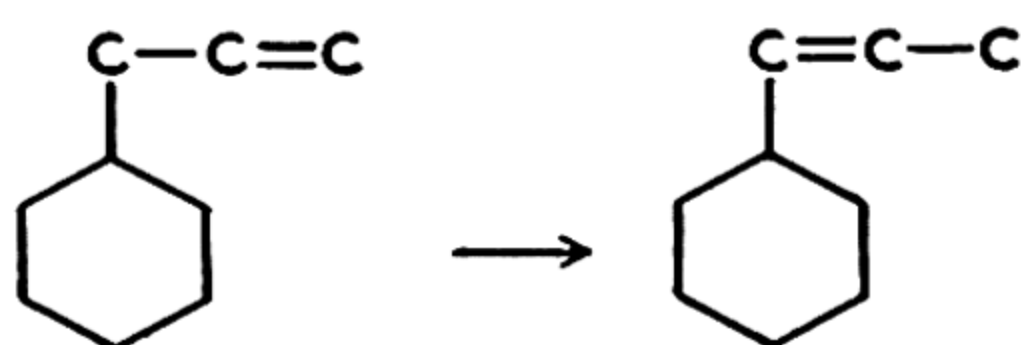
Ethylidenecyclohexane, heated for 6 hours with alcoholic sulfuric acid, formed 1-ethylcyclohexene-1.⁶²⁹ This reaction is probably a general one in the presence of acids:



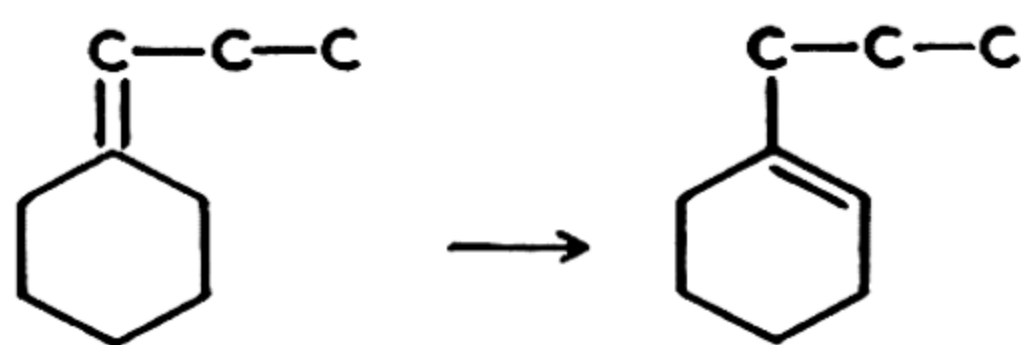
Vinylidenecyclohexane isomerized when heated to 170° with benzoic acid, probably into 1-vinylcyclohexene-1.¹⁶¹ Sodium at $90-100^\circ$ gave sodium cyclohexylacetylide, and cyclohexylethylene.¹⁶¹ The formation of the last hydrocarbon is indicative of hydrogen disproportionation:



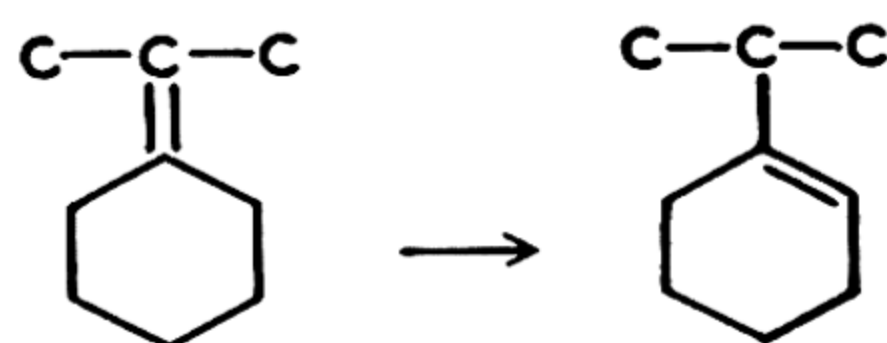
Allylcyclohexane at $500-650^\circ$ gave numerous decomposition products, but probably also formed some propenylcyclohexane:²⁶²



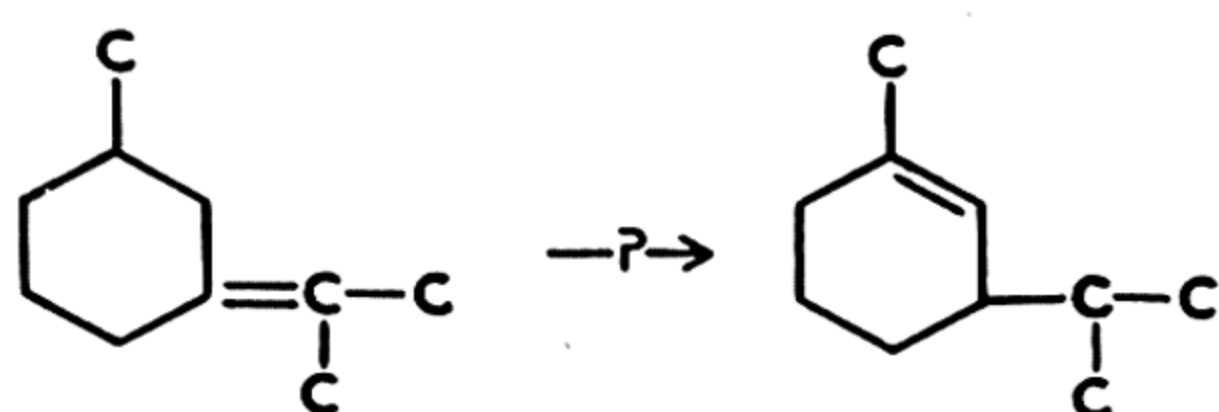
Propylidenecyclohexane, heated 10 hours with alcoholic sulfuric acid, yielded 90 per cent of 1-propylcyclohexene-1:⁶²⁸



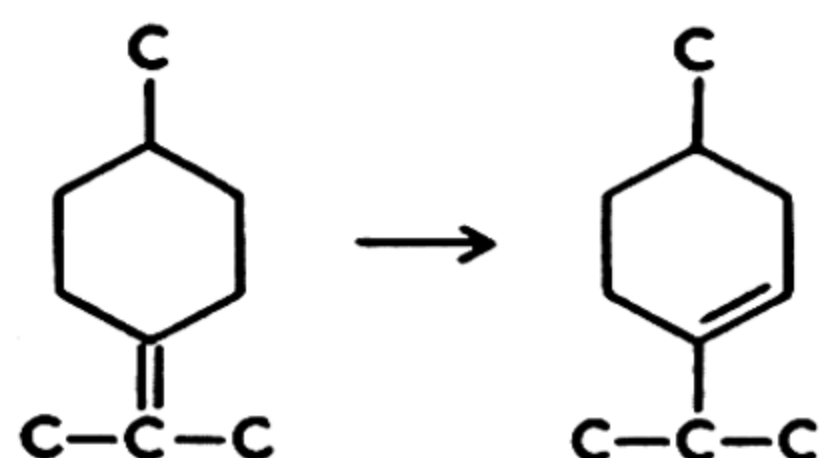
Isopropylidenecyclohexane, heated with alcoholic sulfuric acid, was converted partly into 1-isopropylcyclohexene-1:⁶³¹



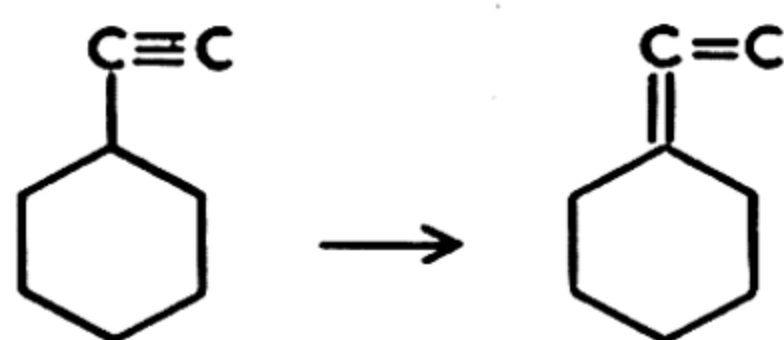
1-Methyl-3-isopropylidenecyclohexane, when heated 10 hours with alcoholic sulfuric acid, gave 20 per cent of an isomer thought to be 1-methyl-3-isopropylcyclohexene-1:⁶²⁷



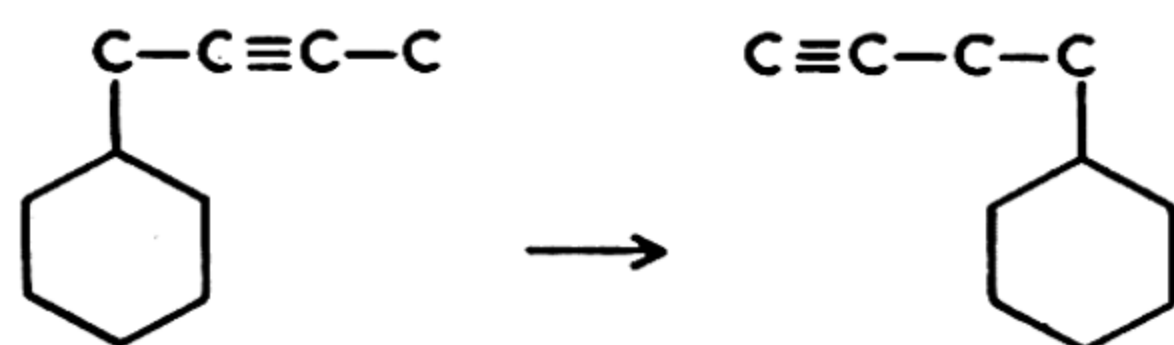
1-Methyl-4-isopropylidenecyclohexane (*i.e.*, $\Delta^{4(8)}$ -menthene; dihydro-terpinolene), heated under reflux for 1 hour with dilute sulfuric acid, gave 1-methyl-4-isopropylcyclohexene-3 (ordinary *dl*-menthene):^{624, 626}



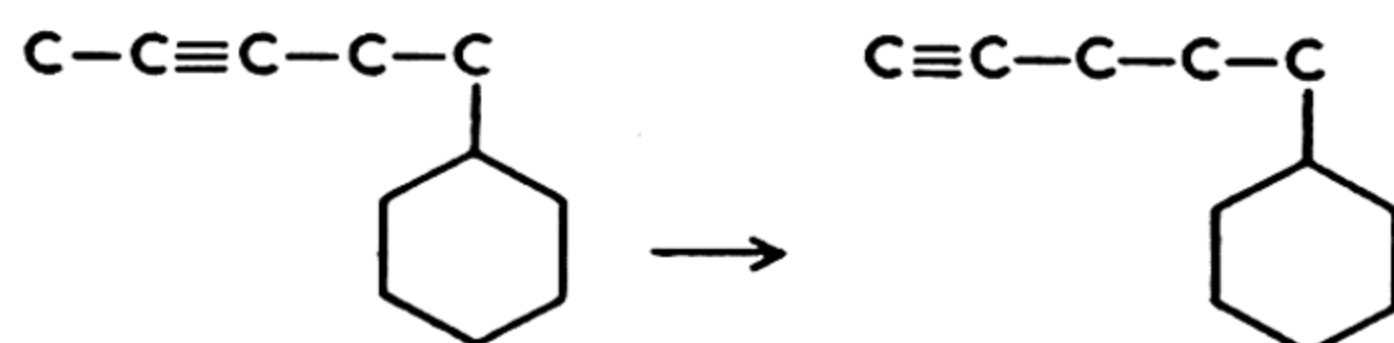
Cyclohexylacetylene isomerized to vinylidenecyclohexane (*i.e.*, cyclohexylideneethylene) under the influence of alcoholic potash at 140°:¹⁶¹



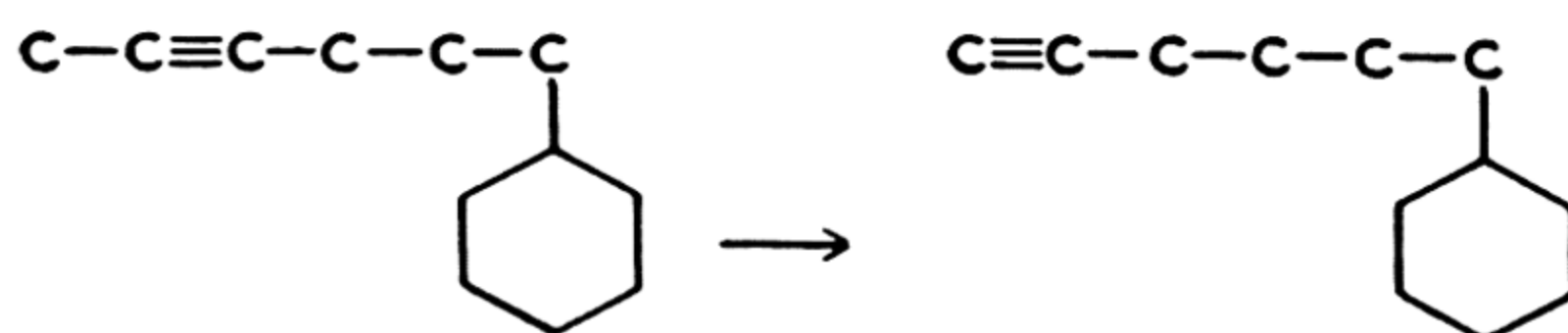
1-Cyclohexylbutyne-2, heated for 3 hours at 160° with sodamide and petroleum, gave 77 per cent of 4-cyclohexylbutyne-1.^{81, 83} The petroleum served to dilute the reactants and to support the sodamide:



5-Cyclohexylpentyne-2, when heated at 160° for 2.5 hours with sodamide and petroleum, formed 76 per cent of 5-cyclohexylpentyne-1:⁸¹



6-Cyclohexylhexyne-2, when heated for 2 hours at 160° with sodamide and petroleum, produced 71 per cent of 6-cyclohexylhexyne-1:⁸¹



Isomerizations of cyclanes with unsaturated side-chains are given in Table 18, p. 304.

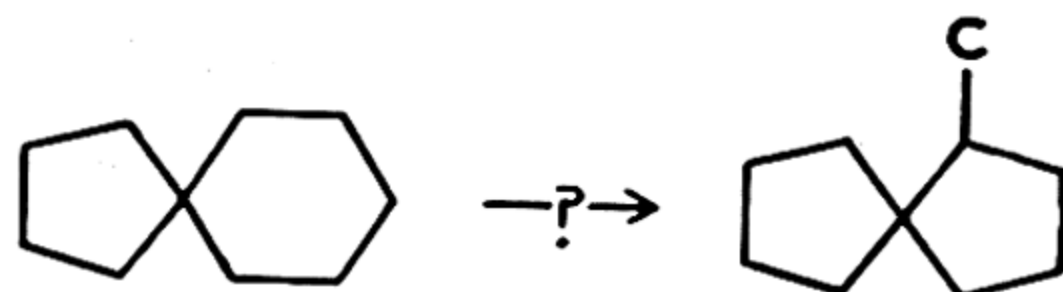
Conclusions

1. Cyclanes with unsaturated side-chains isomerize by changing into alkadienes, cyclenes, or cyclanes having an altered location of unsaturation in the side-chain.
2. The isomerizations exhibited by unsaturated side-chains are subject to the rules of the corresponding unsaturated aliphatic hydrocarbons.
3. Numerous cycloalkylidenes become alkyl cyclenes when treated with acids.

SPIRANES

Isomerizations

The spiranes are a group of hydrocarbons that has been neglected from the isomerization standpoint. Spiro[4.5]decane, however, has been isomerized by slow passage over platinized charcoal at 190° .^{671c} The physical constants of the isomer product (b.p. 185.5 - 186° /750 mm. Hg, $D_4^{20} = 0.8730$, $n_D^{20} = 1.4683$) correspond to those of *trans*-decalin (b.p. 185 - 186.5° , $D_4^{21.5} = 0.8682$, $n_D^{21.5} = 1.4675$), but the product's stability toward dehydrogenation by platinized charcoal at 300° ⁶⁷³ is against this assumption. The isomer may be 1-methylspiro[4.4]nonane:



Further data on isomerization of spiranes are given in Table 19, p. 306.

BICYCLANES AND BICYCLANES WITH SATURATED SIDE-CHAINS

Mechanism

Bicyclanes (bicycloparaffins) and saturated homologs, although extensively encountered in the literature, have been studied only slightly with regard to isomerization. Mechanisms encountered in the previous sections can be applied, but these will require special consideration of the bicyclic structure. Thus, conditions of strain in the molecule to be isomerized may effect geometrical isomerization and changes in ring size. Derivatives of bicyclo[3.1.1]heptane, *i.e.*, of norpinane, exist theoretically in multiplanar strainless forms.²⁰⁵

Isomerizations

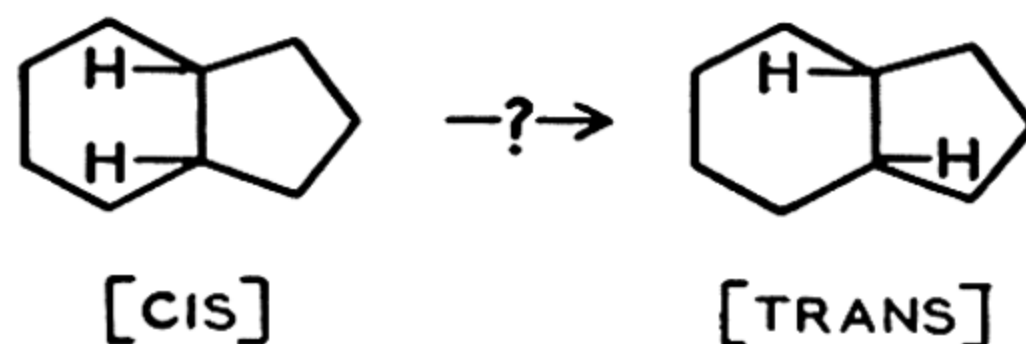
Bicycloheptanes. The isomerization of 2,2,3-trimethylbicyclo[2.2.1]heptane (*i.e.*, dihydrocamphene or isocamphane) by iodine and hydriodic

acid at 240-295° has been reported.³⁵⁴ Starting material and the principal fraction of the product were both mixtures obviously containing impurities; the facts warrant a reëxamination of the reaction.

Bicycloöctanes. Cyclopentane rings in a condensed ring system can be isomerized to cyclohexane rings by the action of aluminum chloride. *Cis*-bicyclo[3.3.0]octane isomerized partly into bicyclo[3.2.1]octane when treated from 2 to 48 hours with aluminum chloride (28.6 per cent) at room temperature.³⁷ This reaction involves, in its over-all aspect, the ruptures of one C—H bond and one C—C bond and a recombination in new directions:



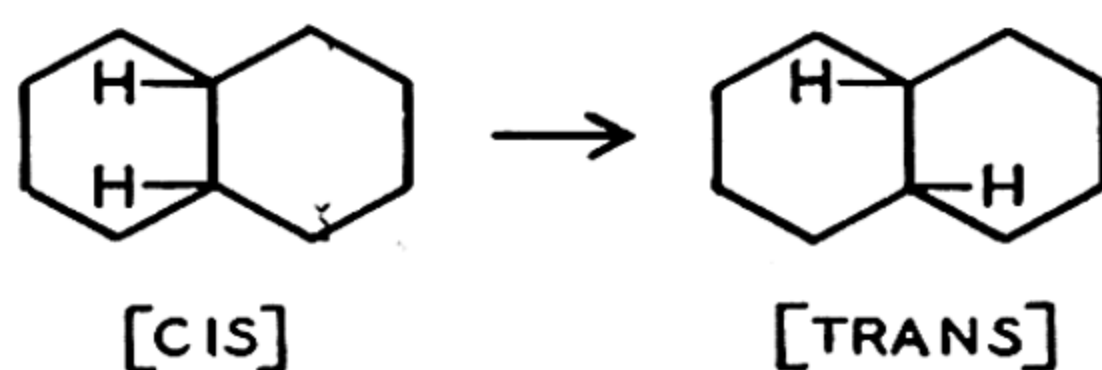
Bicyclononanes. The isomerization of *cis*-bicyclo[4.3.0]nonane (*i.e.*, *cis*-hydrindane), probably into the *trans* form, occurred in 12 hours of treatment at 100° with dry aluminum bromide (43 per cent).⁶⁷⁴ This reaction formed also: an unidentified C₉H₁₆ isomer, a crystalline compound C₂₇H₄₂ (m.p. 192-193°), and an aluminum bromide plus hydrocarbon complex.



Methylhydrindane isomerized to dimethylbicycloöctane in the presence of molybdenum sulfide.²⁹³

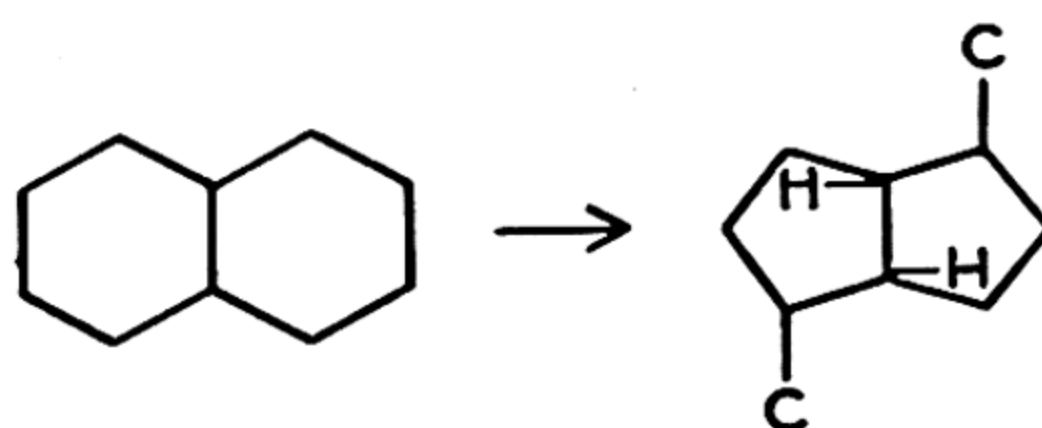
Bicyclodecanes. *Cis*-bicyclo[4.4.0] decane (*i.e.*, *cis*-decalin), treated for 12 hours at 100° with aluminum bromide (25 mole per cent) in the absence of moisture, gave an upper layer containing the *trans* form (about 6 per cent of the theoretical yield) and some isomeric C₁₀H₁₈ (about 4 per cent of the theoretical yield, b.p. 170-175°).⁶⁷³ *Cis*-bicyclo[4.4.0]decane containing dissolved aluminum bromide (31.25 per cent), when subjected to a slow stream of hydrogen bromide, gave an upper layer containing the *trans* form and a lower one of the composition C₁₀H₁₈(AlBr₃)₂.⁶⁷⁴ Further studies⁶⁷⁶ showed that *cis*-bicyclo[4.4.0]-decane, when treated with a technical grade of aluminum chloride at room temperature for 22 hours, gives an 85 per cent yield of the *trans* isomer (b.p. 184.0-186.5°). Heating of the reaction mixture increased the amount of lower-boiling products, as in a reaction of the *cis* form with aluminum chloride (3 moles:1 mole) at 100° for 12 hours. Treatment of the *cis* form for 14 hours at 100° in the presence of a technical grade of aluminum chloride, containing 3 per cent of iron chloride, gave

42.2 per cent of the *trans* isomer (b.p. 184.0-186.5°) and 50 per cent of lower-boiling products. Still later studies⁶⁷⁷ with *cis*-decalin and aluminum chloride at 175-210° gave indications (index of refraction measurements) of *trans*-decalin and a dimethylbicyclo[3.3.0]octane as products. A nickel-cobalt-aluminum alloy has been used to isomerize *cis*-decalin into the *trans* form at 300° under 50 atmospheres' initial pressure of hydrogen.^{545a} *Cis*-decalin, heated with molybdenum trisulfide under hydrogen pressure, gave 40 per cent of *trans*-decalin and 8 per cent of dimethylbicyclo[3.3.0]octane at 425-430°, whereas 52 per cent of the *trans* form resulted at 360-370°:⁴⁴⁹



The heats of combustion of liquid *cis*-decalin and liquid *trans*-decalin at 25° and one atmosphere constant pressure are 1502.4 ± 0.1 and 1500.3 ± 0.1 kilocalories per gram-mole, respectively.^{131b} Subtraction of the second heat quantity from that of the first gives 2.1 ± 0.14 kilocalories per gram-mole as the exothermic heat of isomerization of *cis*-decalin into the *trans* form.

Trans-bicyclo[4.4.0]decane (*i.e.*, *trans*-decalin), when heated with catalysts, undergoes a more severe isomerization, according to later workers. Commercial decalin (75 per cent *trans* form) under the action of aluminum chloride (24.2 per cent) for 24 hours at 130° isomerized partly into *trans*-2,6-dimethylbicyclo[3.3.0]octane (2-5 per cent), and at the same time produced small amounts of monocyclic hydrocarbons.²⁹¹ From 50-70 per cent of decalins were recovered (mainly *trans* form).

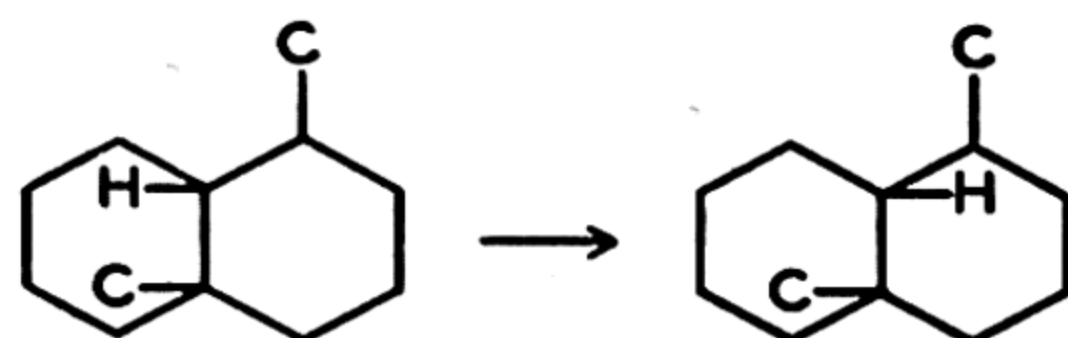


Molybdenum sulfide catalyzed the isomerization of *trans*-decalin into dimethylbicycloöctane at high temperatures.²⁹³

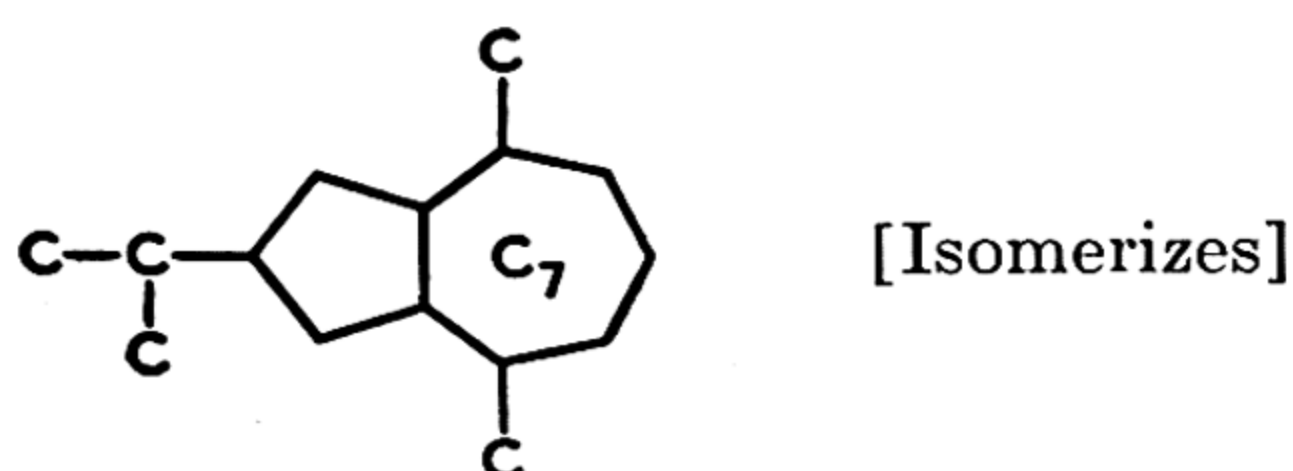
Cis-1-methylbicyclo[4.4.0]decane (*i.e.*, *cis*-9-methyldecalin) formed the *trans* isomer when treated with aluminum chloride at 20°:²⁵²



1,10(or 4,9)-Dimethyldecalin (mainly *cis*), treated with an equal weight of aluminum chloride for 2 days, gave the *trans* form:³⁵¹



2,6 - Dimethyl - 9 - isopropylbicyclo[5.3.0]decane (*i.e.*, β - vetivane) yielded a less strained form upon 3 days' contact with aluminum chloride.^{395b} This product was distinctly different from α -vetivane, which is still another stereoisomer.



The experimental data on isomerization of bicyclanes and bicyclanes with saturated side-chains are given in Table 20, p. 308.

Conclusions

1. Two types of isomerization have been observed in the group of saturated bicyclanes, namely, (a) conversion of *cis* into *trans* forms by rotations at the junction of the 2 rings, and (b) changes in ring size.

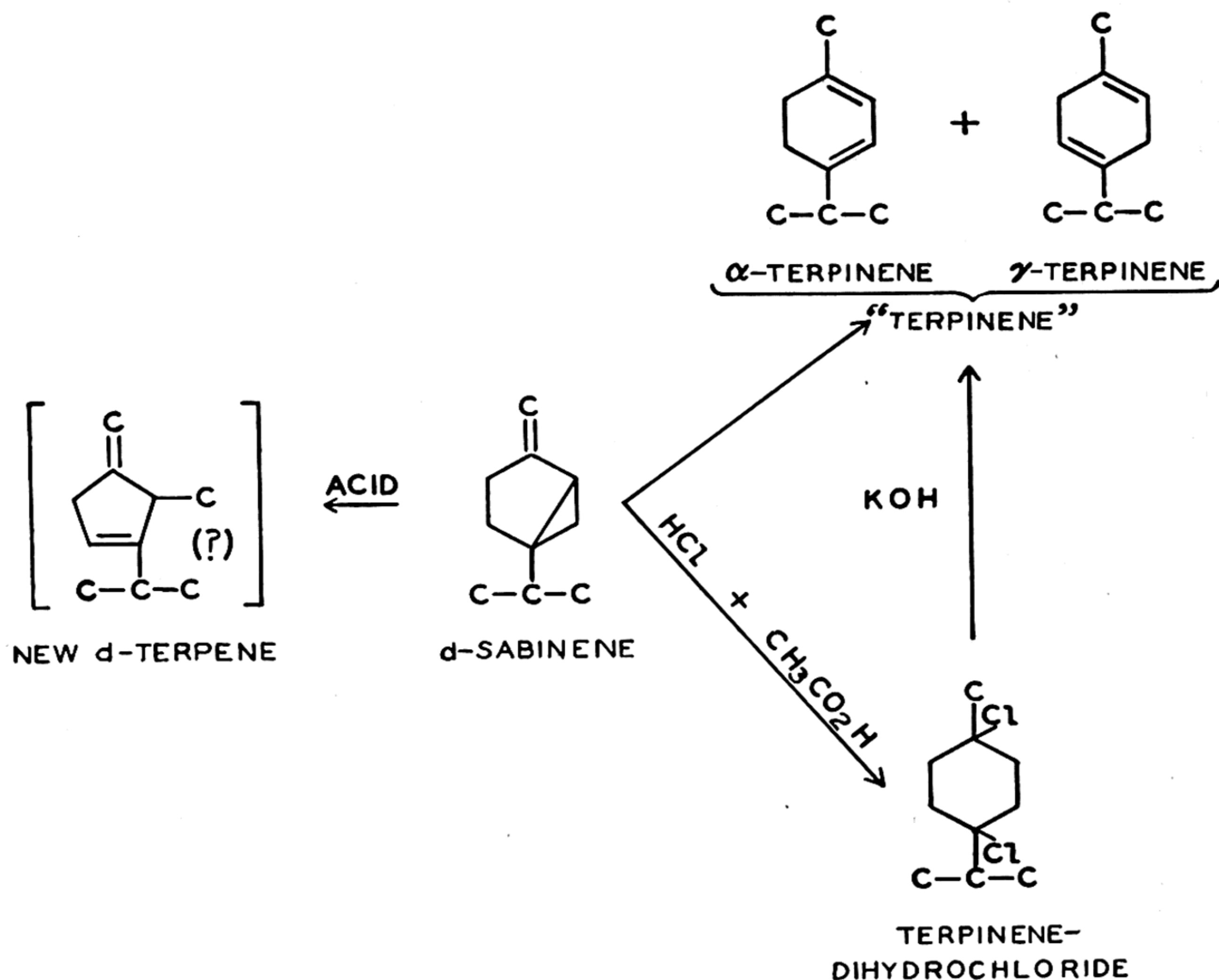
2. Cyclohexane rings within bicyclic hydrocarbons can change into cyclopentane rings, and *vice versa*.

BICYCLANES WITH UNSATURATED SIDE-CHAINS

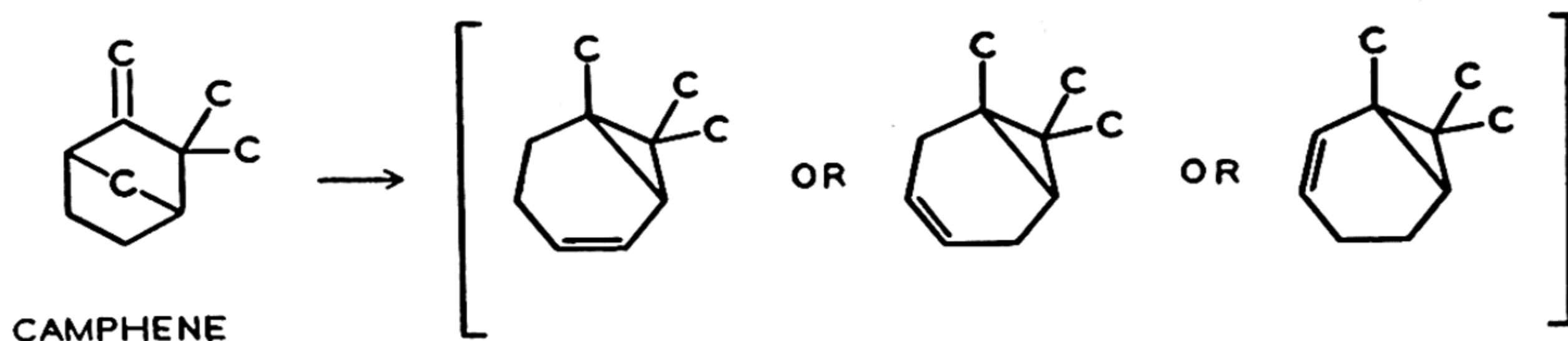
Isomerizations

Bicyclohexanes. *d* - 1 - Isopropyl - 4 - methylenebicyclo[3.1.0]hexane (*i.e.*, *d*-sabinene), heated under reflux with dilute sulfuric acid, formed much α - and γ -terpinenes.⁶²² *d*-Sabinene, heated with either aqueous or alcoholic sulfuric acid, formed also a dextrorotatory five-carbon-ring terpene, probably *d*-1-isopropyl-4-methylene-5-methylcyclopentene-1 (*i.e.*, *d*-1-methylene-2-methyl-3-isopropylcyclopentene-3).⁵³³ The same five-carbon-ring isomer was formed when *d*-sabinene was treated with formic acid at -20° , or with acetic acid plus 50-per cent sulfuric acid at room temperature.⁵³³ Formic acid, and acetic acid plus sulfuric acid, as catalysts,⁵³³ gave also the *d*-monoformate and the monoacetate of terpeneol-4, respectively.⁵³⁴ Sabinene can be converted also into "terpinene" by a

"delayed isomerization" involving formation of terpinene-dihydrochloride and its subsequent dehydrohalogenation.^{621, 622}



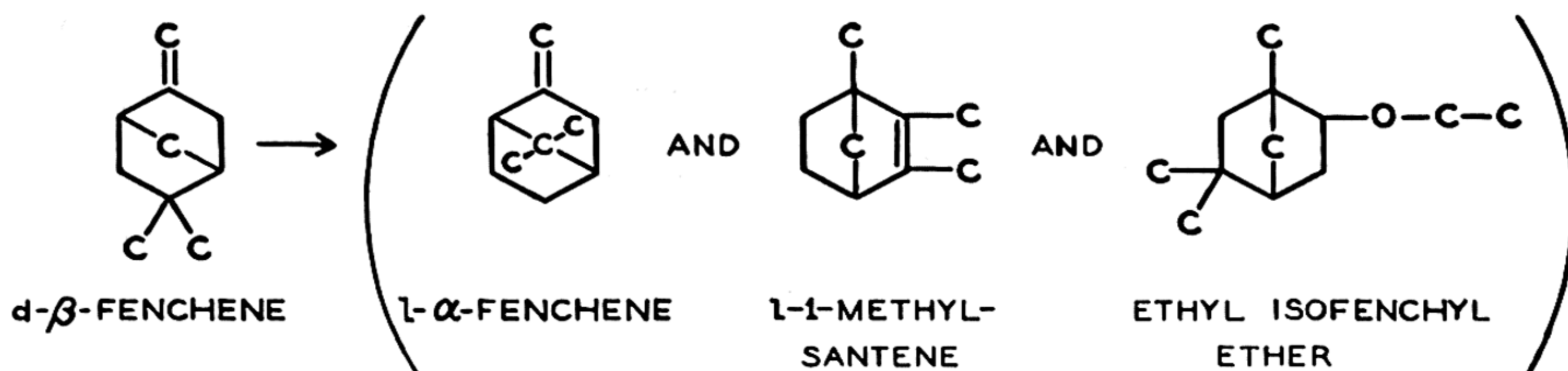
Bicycloheptanes. 2,2 - Dimethyl - 3 - methylenebicyclo[2.2.1]heptane (*i.e.*, camphene) was passed unchanged through a "Suprax" glass tube at 360-370°, which is indicative of its stability.¹² However, camphene when treated with phosphoric acid at 200°, formed an isomer and a diterpene.²⁰¹ Three structures were proposed tentatively for the isomer:



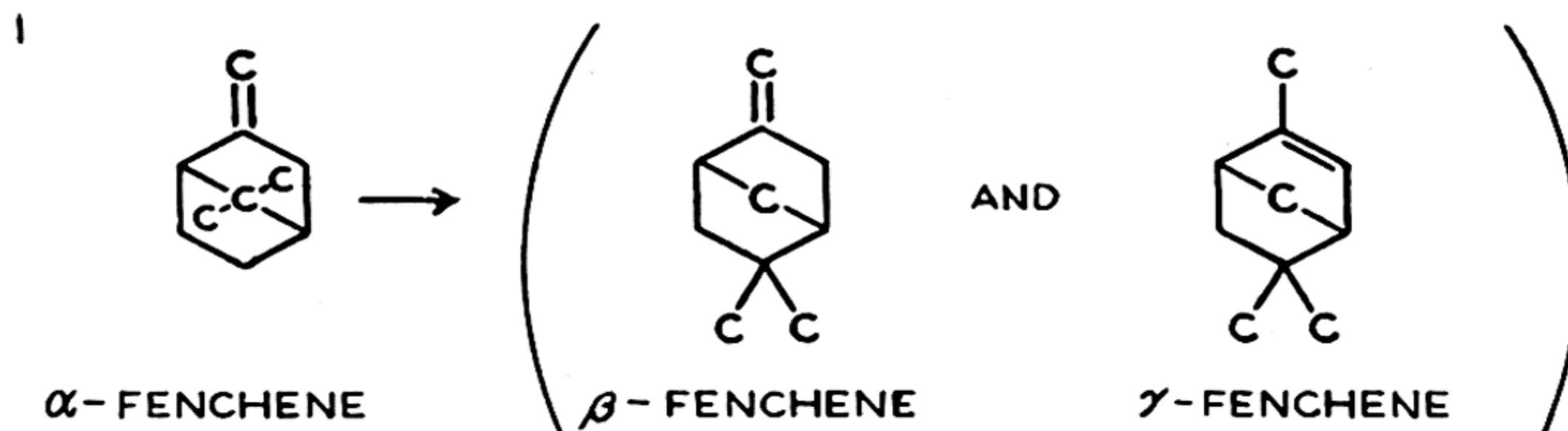
The proposed structures are probably incorrect, since the fused cyclopropane rings (if temporarily formed) would be attacked severely at 200° by the phosphoric acid.

d-2,2-Dimethyl-5-methylenebicyclo[2.2.1]heptane (*i.e.*, *d*- β -fenchene or *d*-2,2-dimethyl-5-methylenenorcamphane), heated under reflux with ethanol containing a small amount of dilute sulfuric acid or some potas-

sium hydrogen sulfate, underwent isomerizations to *l*-2-methylene-7,7-dimethylbicyclo[2.2.1]heptane (*i.e.*, *l*- α -fenchene or *l*-2-methylene-7,7-dimethylnorcamphane) and *l*-1,2,3-trimethylbicyclo[2.2.1]heptene-2 (*i.e.*, *l*-1-methylsantene or *l*-1,2,3-trimethylnorcamphene-2).^{320a} Ethyl isofenchyl ether was formed in considerable amounts as a by-product. These isomerizations involve Wagner-rearrangements:*



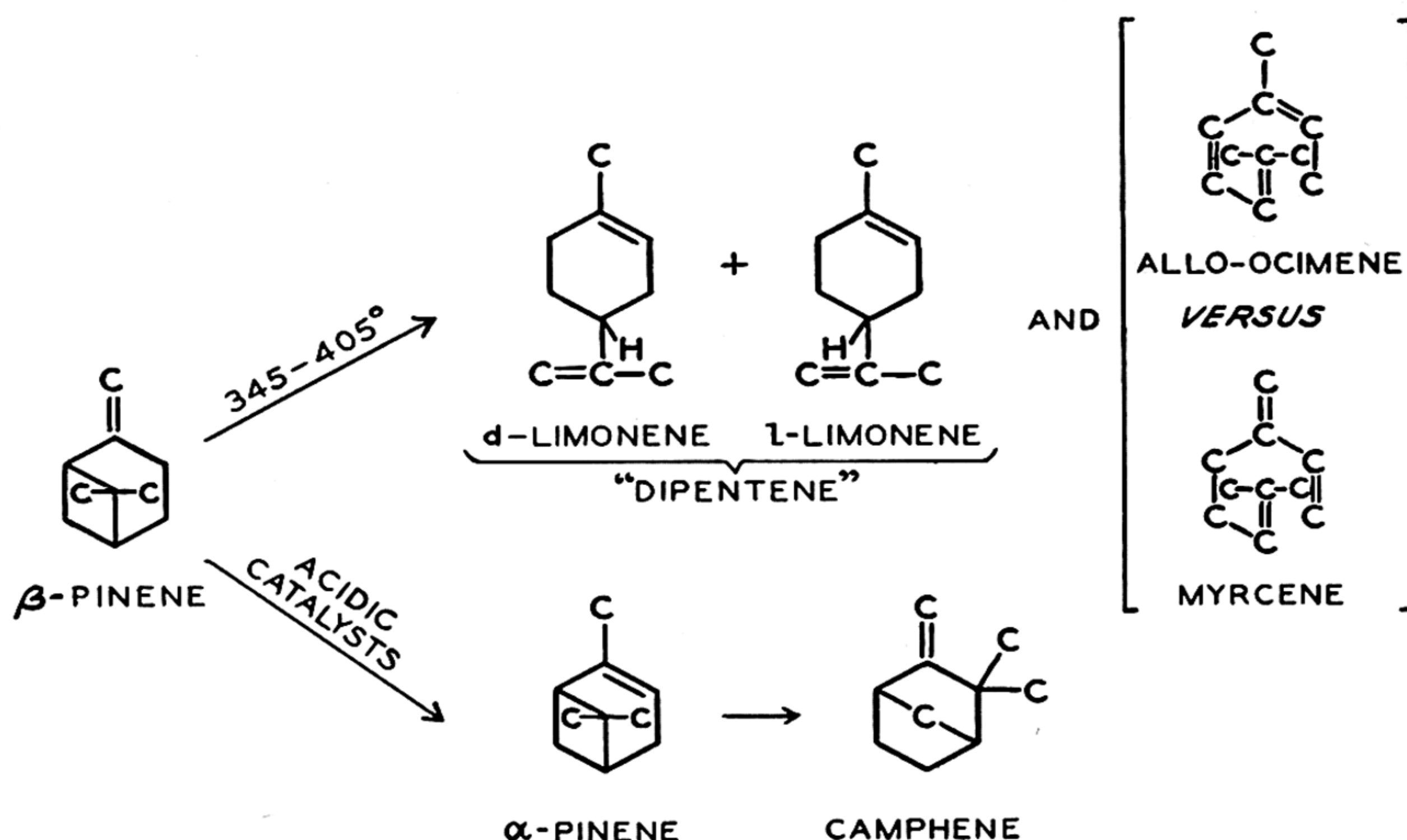
dl-2Methylene-7,7-dimethylbicyclo[2.2.1]heptane (*i.e.*, *dl*- α -fenchene) was completely isomerized to a mixture of 2,2-dimethyl-5-methylenebicyclo[2.2.1]heptane (*i.e.*, β -fenchene) and 2,5,5-trimethylbicyclo[2.2.1]heptene-2 (*i.e.*, γ -fenchene or 2,5,5-trimethylnorcamphene-2) by a 7-15 minutes' treatment with potassium hydrogen sulfate at the boiling point of the mixture:^{320a}



2-Methylene-6,6-dimethylbicyclo[3.1.1]heptane (*i.e.*, β -pinene or nopinene) when passed through a "Suprax" tube at 345-350° gave alloocimene (25 per cent) dipentene, and some unconsumed β -pinene.¹² This reaction is related closely to the isomerization of α -pinene into alloocimene (considered later). Recent work^{217b} indicates that *l*- β pinene is converted at 400-405° into *l*-limonene, myrcene, α -camphorene, and other polymers of myrcene. No evidence was obtained for an isomerization to allo-ocimene. Numerous acidic catalysts are known which convert β -pinene successively into α -pinene and then into camphene.^{459a, 502, 503, 504,}

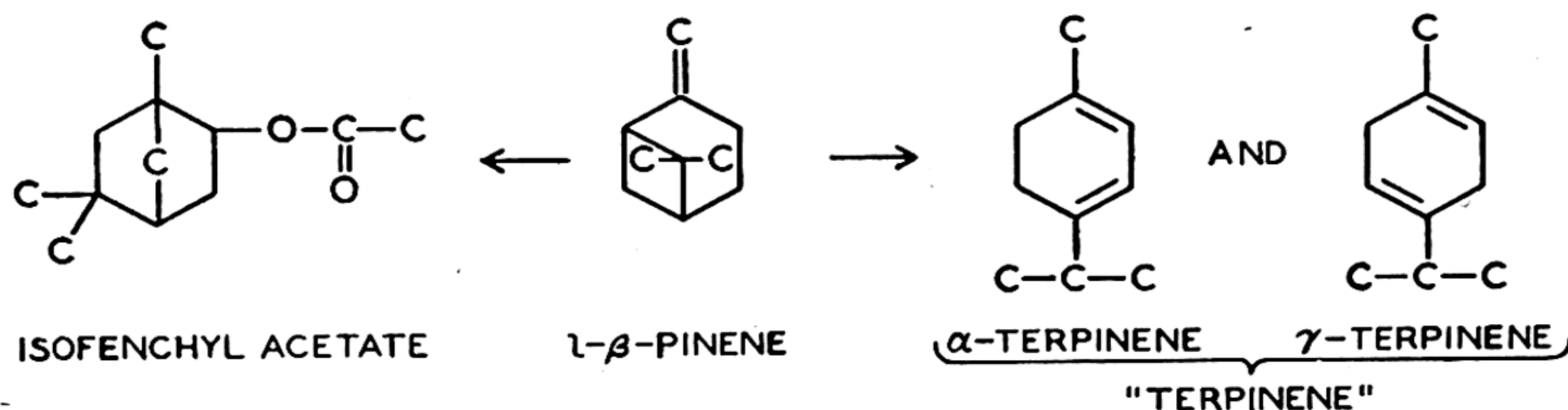
* The following structural formulas for α -, β -, and γ -fenchenes, 1-methylsantene, and ethyl isofenchyl ether are oriented so that the 2 uppermost carbon atoms are immobile, which enables a comparison to be made with the structure of cyclofenchene (*supra*). The last hydrocarbon may be considered as a probable intermediate for the given examples of isomerization, but its present non-isolation seems to indicate the operation of a mobile system of diyl forms, such as 1,3,3-trimethyl-tricyclo[2.2.1.0^{2,6}]hepta-2,6-diyl, rather than a closed, true tricyclic structure.

504a, 508, 508a, 509, 510, 511, 511a, 512a, 513, 514, α -Pinene is considered to be a less strained molecule than β -pinene.²⁰⁴



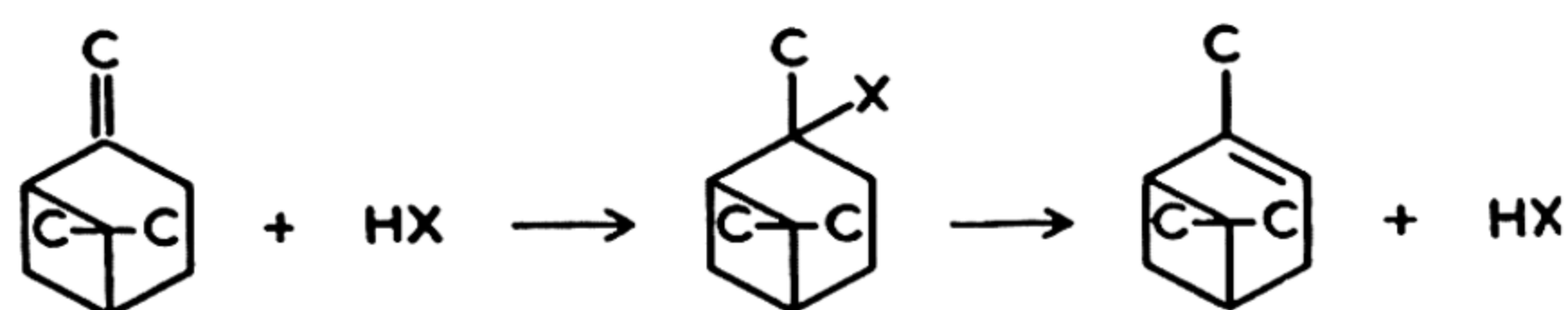
l- β -Pinene, treated with palladium black and hydrogen at room temperature, undergoes isomerization by double-bond shift, forming *l*- α -pinene.⁴⁶⁶ This reaction is irreversible, since similarly treated *l*- α -pinene does not undergo isomerization.^{466, 663}

β -Pinene, heated under reflux for 1.5 hours with fuller's earth, gave "terpinene" and a polymer called "dipinene."⁶¹⁰ *l*- β -Pinene, when heated for one hour at 60° with acetic plus sulfuric acid, gave "terpinene" (b.p. 175-180°, hence the mixture of α - and γ -terpinenes), and a small amount of isofenchyl acetate.⁶²⁵ The last ester was considered as the intermediate probably responsible for the terpinenes, but the authors are inclined to consider the presence of this acetate as incidental to a formation of α -fenchene, giving cyclofenchene or even δ -fenchene.



l- β -Pinene, heated with benzoic acid at temperatures "below 145°," gave α -pinene without bornyl esters.¹⁹ However, bornyl benzoate, *l*-limonene, and *l*- α -pinene were formed at 125°, ²¹ and 14 per cent of bornyl benzoate accompanied the α -pinene formed at 125-130°. ²⁰ Moreover, β -pinene, when treated with "organic acids" at 140-150°, led to α -pinene

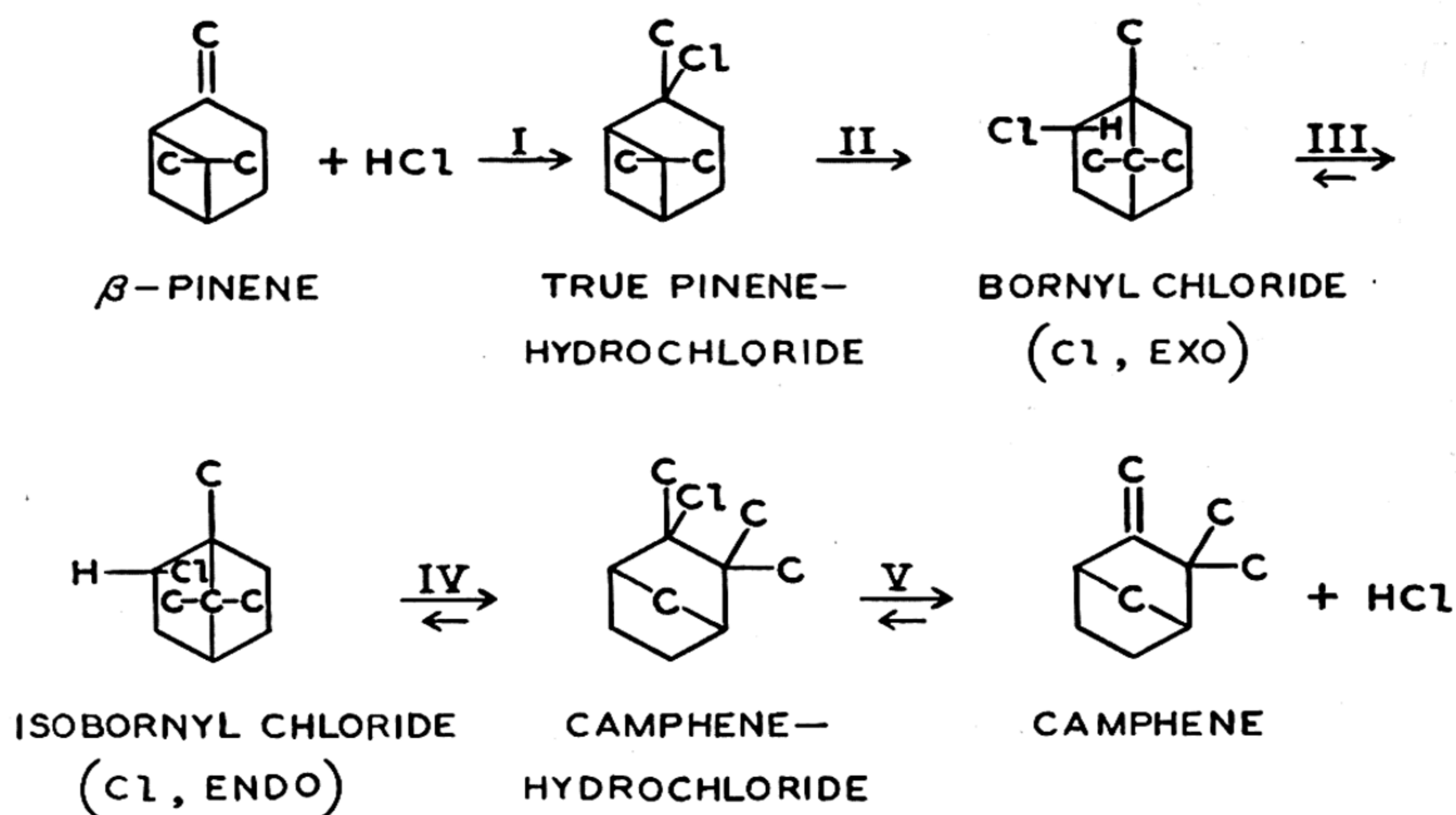
plus bornyl and isobornyl esters.¹⁸ Treatment of *l*- β -pinene at 160° for 12-20 hours with salicylic acid, which is a considerably stronger acid, gave 50 per cent of terpenes, consisting of limonene, *l*- α -pinene and "terpinene," and 35-36 per cent of bornyl esters.¹⁹ The use of trichlorophenol for 30 hours at 145° resulted in a large conversion into *l*- α -pinene, along with traces of bornyl and fenchyl esters.¹⁹ The conversions were formulated as follows:¹⁹



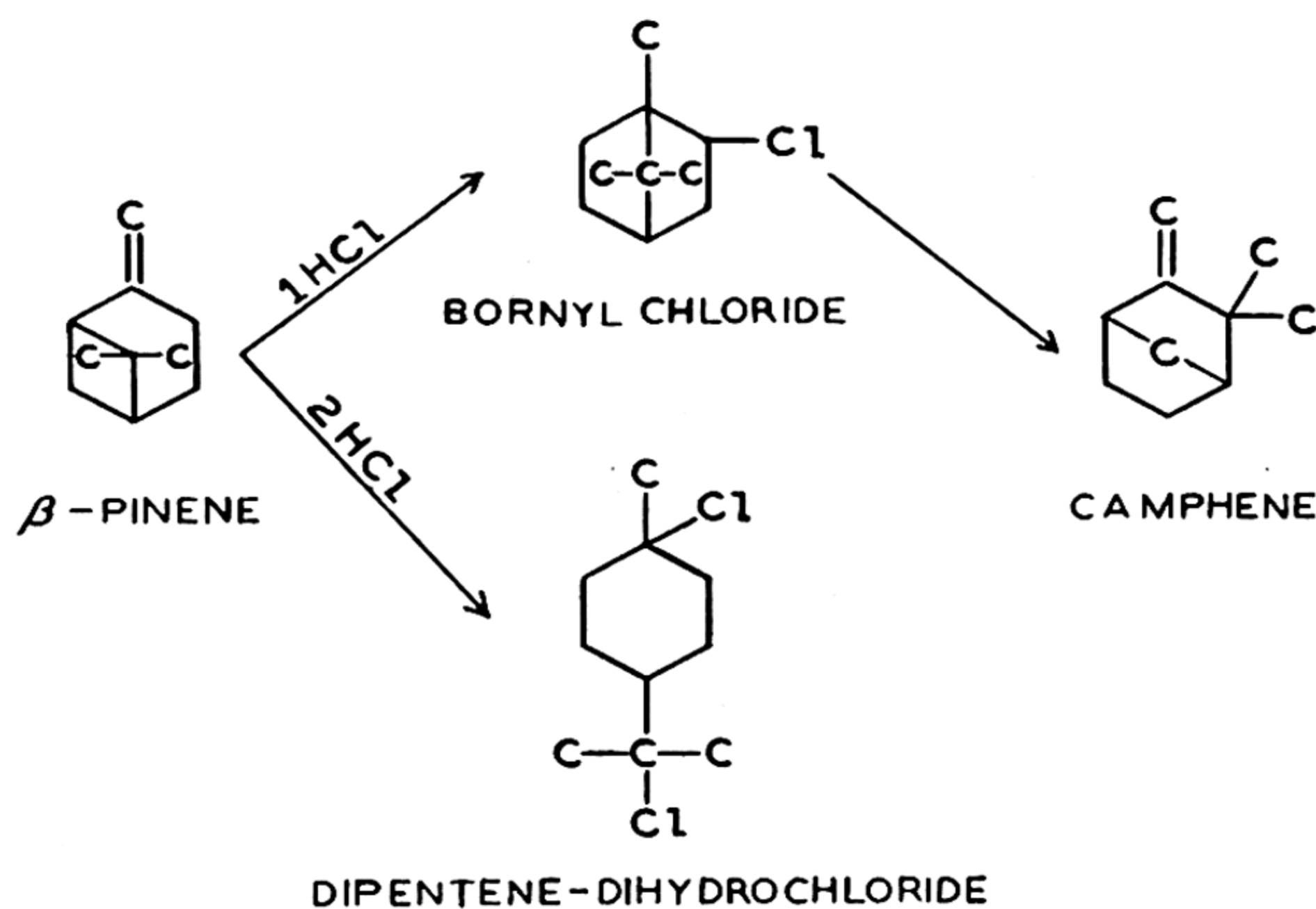
Some related preliminary work on β -pinene plus picric acid has been reported also.³²² *l*- β -Pinene, picric acid, plus benzene at 120° gave *l*-camphene, *l*-limonene, *l*- α -pinene, and 4 esters.¹³³ *l*- β -Pinene, heated 30 hours either with stearin at 145° or with colophony at "160-100°," yielded 70 per cent of *l*- α -pinene.²⁰

l- β -Pinene, heated at 130-180° for 10 or 20 hours with abietic acid, formed camphene and *l*- α -pinene.¹⁹ The formation of camphene from β -pinene, an "unusually delayed isomerization" via acids, involves a double Wagner rearrangement: that of β -pinene into bornyl esters⁶²⁵ and of isobornyl into isocamphanyl esters.^{369, 370} With hydrogen chloride, the first step is the formation (at -15°) of the exceedingly unstable true pinene-hydrochloride.¹⁷ The latter isomerizes quickly (at 10°) into the relatively stable bornyl chloride.³⁷⁰ Bornyl chloride, heated at 100°, undergoes a transformation into its less-stable stereoisomer, isobornyl chloride.* Still higher temperatures (125°) convert the isobornyl chloride into camphene hydrochloride, which is an isocamphanyl ester noted for its ready dissociation into camphene and hydrogen chloride^{369, 370} The general reversibility of this system of chlorides decreases in the direction camphene to β -pinene. Camphene hydrochloride dissociates readily³⁹ into camphene and hydrogen chloride, whereas true pinene-hydrochloride quickly and irreversibly forms bornyl chloride.^{17, 370} The transformation of β -pinene into camphene, via acids and acidic catalysts, proceeds apparently in 5 steps, according to the following "right-shift" of reactions:

* The Wagner rearrangements require the chlorine atoms of bornyl chloride and isobornyl chloride to be located respectively *exo* and *endo* to the opposite side of the non-planar or partly collapsed hexagon. These structural arrangements bring the chlorine atom of true pinene-hydrochloride and of bornyl chloride into actual proximity to the dimethylmethylen bridge and similarly place the chlorine atoms of isobornyl chloride and camphene hydrochloride in an advantageous mid-position. The present assignment is in agreement with that of Bredt^{90a, 71a, 88a, 353b, 355a, 355b} and contrary to the proposals of Vavon and others.^{2a, 2b, 15a, 15b, 257c, 258a, 319a, 609b, 609c}



l- β -Pinene, treated in the cold with dry ether (or acetic acid) saturated with hydrogen chloride, gives a mixture of *l*-bornyl chloride and dipentene dihydrochloride.⁶²⁵ Bornyl chloride yields camphene when heated at 190-200° for 4 hours with anhydrous sodium acetate and acetic acid in a bomb tube.^{617, 625}



The isomerizations of bicyclanes with unsaturated side-chains are given in Table 21, p. 310.

Conclusions

1. Bicyclanes with unsaturated side-chains isomerize to the following products: alkatrienes, alkenyl cyclenes, cyclodienes, isomeric bicyclanes with unsaturated side-chain and with same ring sizes, bicyclanes with unsaturated side-chain and different ring sizes, bicyclenes with same ring sizes, or bicyclenes with different ring sizes.

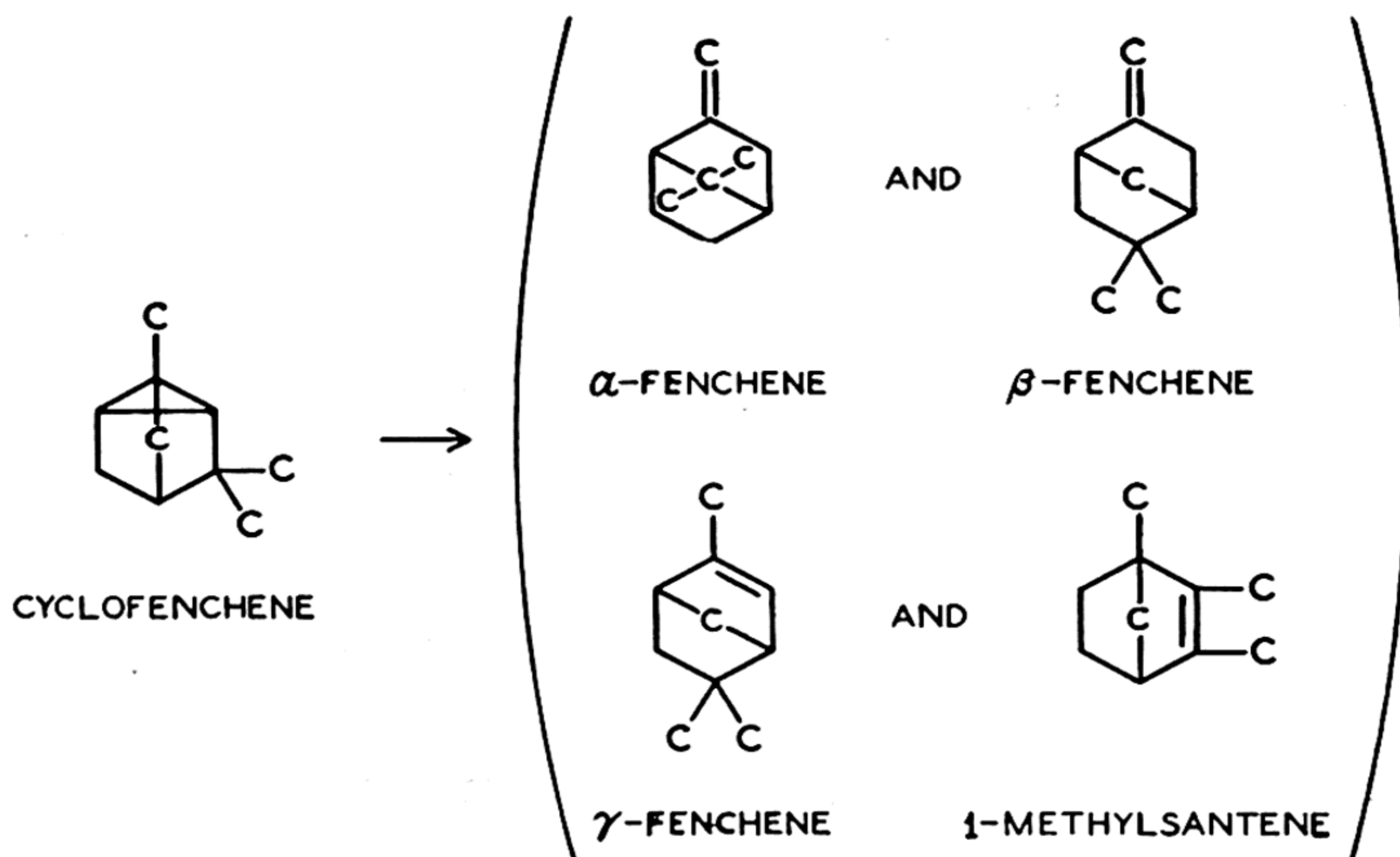
2. Formation of a cyclodiene involves both decyclization and a shift of side-chain double bond into the remaining ring.

3. Formation of a bicyclene, from β -pinene, is an easy, more-or-less direct, transformation proceeding even at room temperature, whereas the formation of an isomeric bicyclane with unsaturated side-chain (camphene) should be considered as a complex process.

TRICYCLANES

Isomerizations

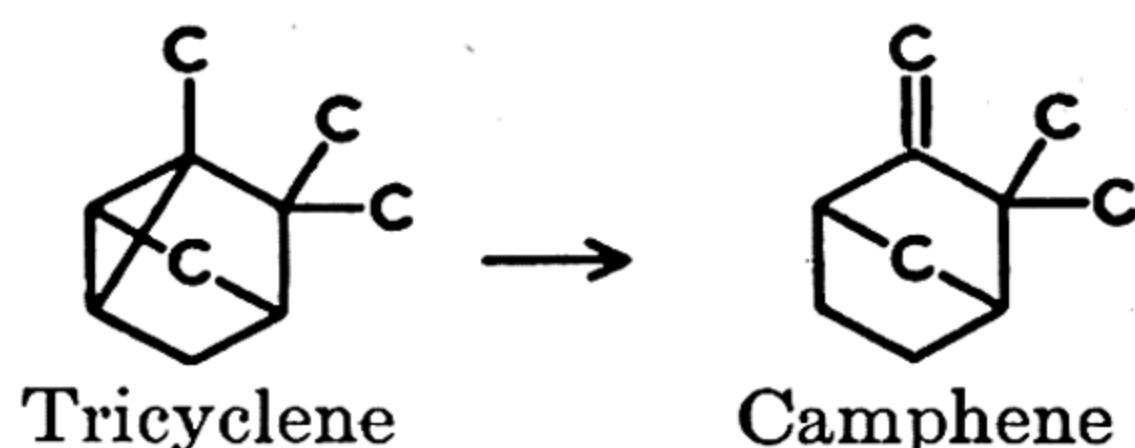
1,3,3-Trimethyl-tricyclo[2.2.1.0^{2,6}]heptane (the tricyclic* terpene "cyclofenchene") isomerizes by rupture of one of 3 bonds comprising a cyclopropane ring, with formation of α -, β -, and γ -fenchenes and 1-methylsantene. An isomerization into α - and β -fenchenes occurred in the presence of platinized charcoal at 300°. ⁶⁶⁹ Heating of cyclofenchene with potassium acid sulfate or phthalic anhydride gave β - and γ -fenchenes, ³²⁰ whereas concentrated phosphoric acid ³²⁰ and activated "Florida earth" ⁵⁸⁷ formed 1-methylsantene (i.e., 1,2,3-trimethylnorcamphene-2). The formation of 1-methylsantene ⁵⁸⁸ can be looked upon as a "retropinacol rearrangement," which occurs in preference to formation of δ -fenchene. The formation of β - and γ -fenchenes, as a pair of products, calls for the presence of 2,7,7-trimethylnorcamphene-2 whenever α -fenchene is formed. However, neither 2,7,7-trimethylnorcamphene-2 nor 5,7,7-trimethylnorcamphene-2 (another possibility) has been reported to date:



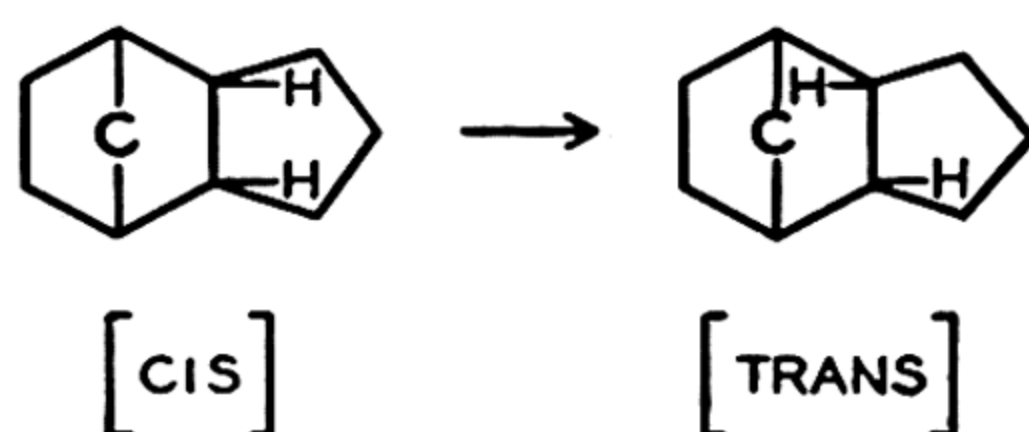
2,3,3-Trimethyl-tricyclo[2.2.1.0^{2,6}]heptane (the tricyclic terpene "tricyclene") isomerizes to *dl*-camphene by rupture of one bond and migration of a hydrogen atom. This isomerization occurred both upon heat-

* The "cyclohexane" rings of cyclofenchene, tricyclene, and tetrahydro-di-cyclopentadiene are not to be construed as established or additional rings. They are assumed to be physically non-existent and to be adequately defined as two cyclopentane rings of fused type.

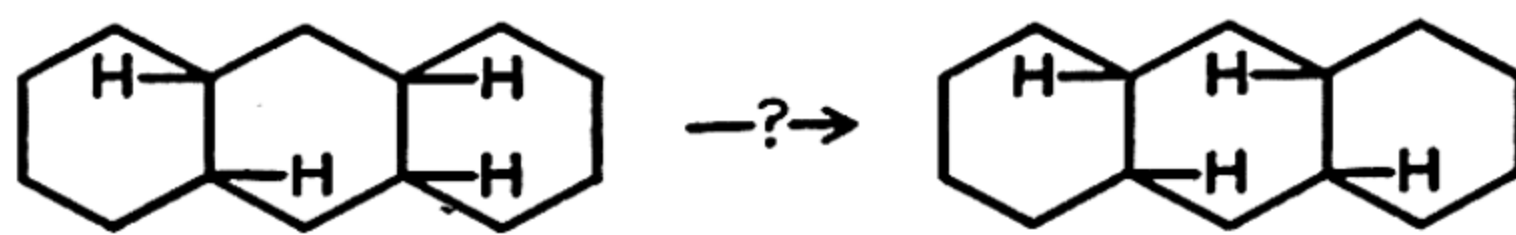
ing with sodium hydrogen sulfate at 168° ³⁵⁵ or upon passage over nickel at $180-200^{\circ}$ in a slow current of nitrogen.³⁶⁹



Tricyclo[5.2.1.0^{2,6}]decane (*i.e.*, tetrahydro-di-cyclopentadiene) probably exists in *cis* and *trans* forms.¹⁶² Unfortunately, structural errors are to be found in the literature, due to a prolonged controversy over the constitution of "dicyclopentadiene."¹⁵⁷ Long heating of tricyclodecane (m.p. 77°) with sulfuric acid containing a small amount of pyrosulfuric acid, at a temperature somewhat above 77° , gave a stereoisomer of m.p. 9° .¹⁶² This isomerization may be formulated as a conversion of the *cis*-tricyclodecane into its *trans* form:

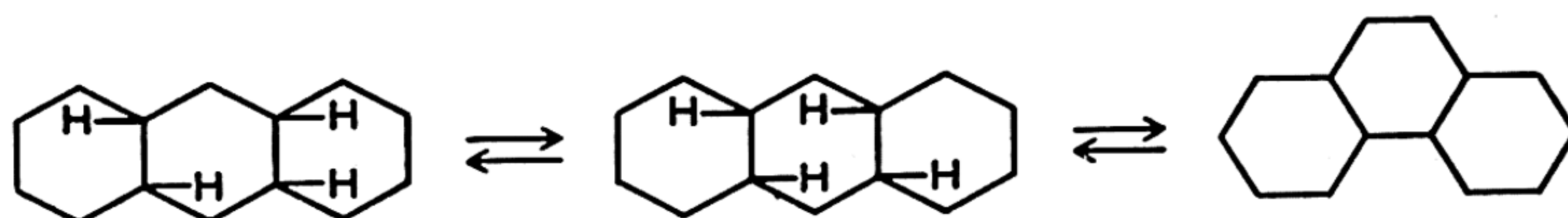


Prolonged heating of "liquid" tetradecahydroanthracene at 270° in the presence of nickel and hydrogen under high pressure gave "solid perhydroanthracene." This is apparently an isomerization of a labile liquid form and may be a conversion of 3,8-*cis*-1,10-*trans*-tricyclo[8.4.0.0^{3,8}]tetradecane into 1,10-*trans*-3,8-*trans*-tricyclotetradecane:⁶³⁷



A similar reaction occurred when "liquid" tetradecahydroanthracene was treated at 100° with aluminum chloride, or with molybdenum trisulfide under hydrogen pressure at $330-380^{\circ}$.⁴⁵¹

"Solid" tetradecahydroanthracene plus compressed hydrogen formed some tetradecahydrophenanthrene when heated at 460° with or without molybdenum trisulfide, whereas treatments with aluminum chloride at 100° without hydrogen probably gave mixtures of "liquid" tetradecahydroanthracene plus tetradecahydrophenanthrene:⁴⁵¹



Tetradecahydrophenanthrene was converted partly into "solid" tetradecahydroanthracene when subjected either to aluminum chloride at 100° or to molybdenum trisulfide and hydrogen under pressure at 380°. ⁴⁵¹ Tetradecahydrophenanthrene is a tricyclo[8.4.0.0^{4,9}]tetradecane with interesting stereochemical possibilities. ³⁵²

Isomerizations of tricyclanes are given in Table 22, p. 316.

Conclusions

1. The isomerizations of cyclofenchene and tricyclene indicate that cyclopropane rings (comprising a part of tricyclanes) can be expected to open readily. The products formed are bicyclanes with an unsaturated side-chain, or bicyclenes.

2. The isomerization of tricyclanes from *cis* into *trans* forms can be expected on account of their close relationship to the saturated bicyclanes.

PENTACYCLANES

l- α -Cryptomerene, obtained from the *Cryptomeria japonica*, is a diterpene (C₂₀H₃₂) of unknown structure. Treated with anhydrous hydrogen chloride in the presence of well-cooled ether, it gives β -cryptomerene. ⁶⁰¹ These isomers can be considered as pentacyclanes, since neither combines with hydrogen chloride or iodine. ⁶⁰¹

Chapter V

Cyclenes, Bicyclenes, and Polycyclenes

The isomerizations of cyclenes, bicyclenes, and polycyclenes (*i.e.*, the cycloölefins) are discussed in the following order: cyclenes and cyclenes with saturated side-chains, cyclenes with unsaturated side-chains, cyclodienes with saturated side-chains, cyclodienes with unsaturated side-chains, bicyclenes and bicyclenes with saturated side-chains, bicyclenes with unsaturated side-chains, bicyclodienes with saturated side-chains, tricyclenes and tricyclenes with saturated side-chains, tricyclenes with unsaturated side-chains, tetracyclenes, and pentacyclenes.

The isomerizations of the cyclenes contain several examples in the sesquiterpene group $C_{15}H_{24}$, wherein structures of many members are unknown. The concept of molecular refraction, and of its exaltation due to the influence of conjugated double bonds, has been of value in elucidating structures of the sesquiterpenes.⁴⁹⁰ These concepts should be used more often in the entire cyclene series of hydrocarbons. The sesquiterpenes include aliphatic members with 4 double bonds, monocyclics with 3 double bonds, bicyclics with 2 double bonds, tricyclics with one double bond, and possibly saturated tetracyclics. Usually, these members occur as a mixture in which the double bond is unlocated. The isomerization of the aliphatic sesquiterpenes has been discussed in Chapter II, under "Alkapolyenes."

Typical examples of isomerization among the diterpenes ($C_{20}H_{32}$) are the conversions of α -camphorene, phyllocladene, and sclarene into isomers. The diterpenes theoretically comprise aliphatic, and monocyclic to pentacyclic members, all of which can be considered as isoprene tetramers, each of which has a different degree of cyclization. Isomerization of these members consists usually of alterations in both degree of cyclization and location of double bonds. Variation of the size of rings, aromatization, and transformations in the side-chain are still other types of isomerization possible in diterpenes. Again, the known structures of the terpenes, sesquiterpenes, and diterpenes, as isoprene polymers, further suggest a possible partial depolymerization followed by recombination to an isomer.

The isomerization mechanisms of cyclenes will be discussed for members having special characteristics due to their structures or reaction conditions. Explanations of isomerization that have been given in pre-

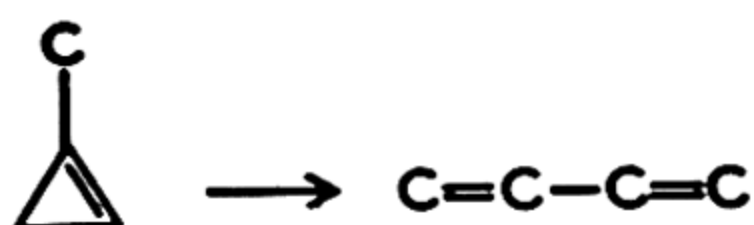
ceding sections are generally applicable to movements of double bonds, cyclization and decyclization occurring within the various cyclenes.

CYCLONES AND CYCLENES WITH SATURATED SIDE-CHAINS

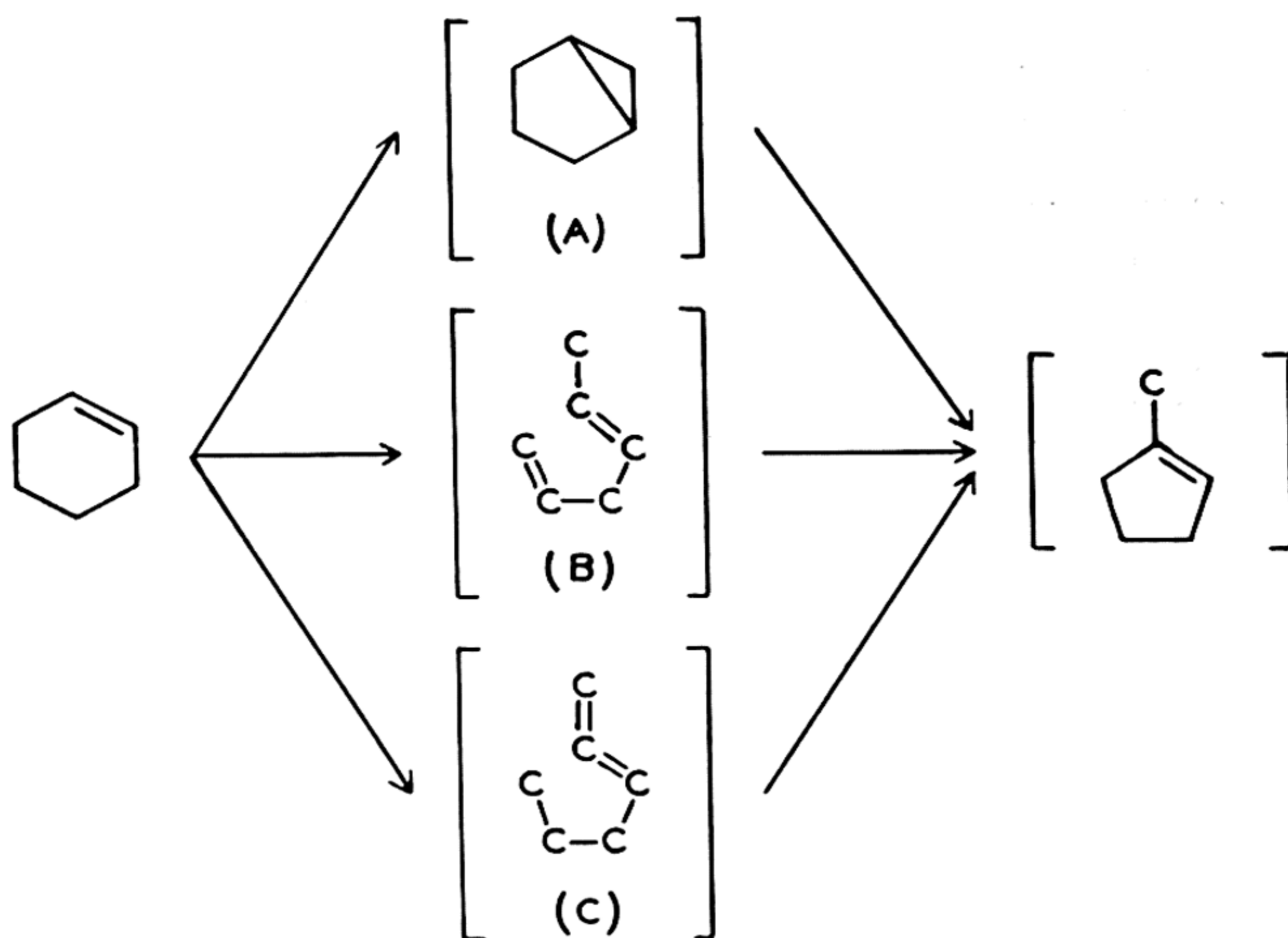
The cyclenes with saturated side-chains or without side-chains comprise the simplest group of all cyclenes. Nevertheless, only a few examples of isomerization in this group are known. The movement of saturated side-chains *per se* has not been observed, which may be due to the possible existence of equilibria favoring: shifts of the double bond, decyclization, or decyclization plus cyclization.

Isomerizations

1-Methylcyclopropene-1, passed over alumina at 325°, gave butadiene-1,3.³⁷³ The product contained isobutene, originally present in the 1-methylcyclopropene-1.



Cyclohexene passed once over silica gel at 400° or 450°, or twice over heated alumina, formed "methylcyclopentene."⁶⁶⁵ Isolation of methylcyclopentane, when the catalyzate was subjected to (a) hydrogenation, (b) selective dehydrogenation of the cyclohexane, and (c) elimination of benzene, was given as indirect evidence of isomerization. These experiments do not prove that methylcyclopentenenes were present in the catalyzate to the exclusion of methylenecyclopentane. Bicyclo-[3.1.0]hexane (A) was proposed as an intermediate product, but hexadienes (B) (C) are also possible intermediates:



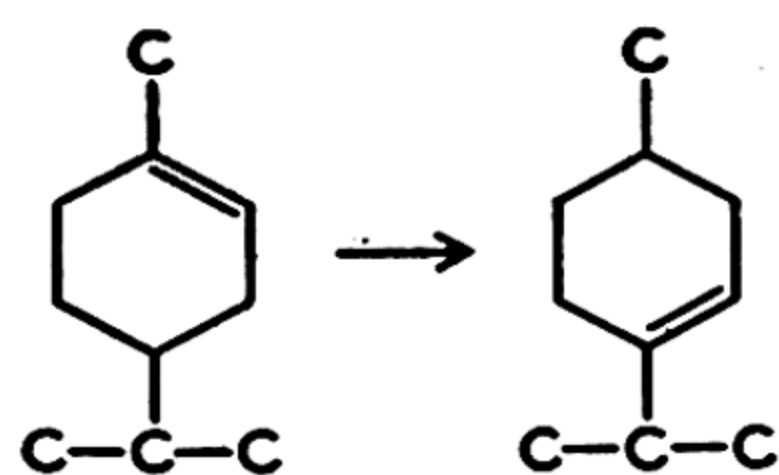
The passage of cyclohexene over a phosphoric acid-on-silica catalyst at 350° yielded about 64 per cent of a "methylcyclopentene."^{529a}

Conduction of cyclohexene over titanium dioxide, at 350° followed by re-treatment of the main condensate, or singly at 400° or 450°, gave about 19, 18, and 11 per cent, respectively, of "methylcyclopentene."^{12a} Passage of cyclohexene over beryllium oxide at 450°, with one recycle of the condensate's main fraction, yielded approximately 48.2 per cent of "methylcyclopentene."^{12a} The four preceding "methylcyclopentene" percentages are based upon the final yields of methylcyclopentane obtained from the stated cyclohexene plus "methylcyclopentene" fractions by (a) hydrogenation over platinized charcoal at 150° to form cyclohexane plus methylcyclopentane, (b) selective dehydrogenation of the cyclohexane over the same catalyst at 300°, giving a benzene plus methylcyclopentane mixture, and (c) elimination of benzene by treatment with fuming sulfuric acid. "Methylcyclopentene" has been suggested as one intermediate in the pressure hydrogenation of cyclohexene over molybdenum disulfide (MoS_2), since some methylcyclopentane accompanies the cyclohexane formed.^{408a}

1-Methylcyclohexene-1, heated with a mixture of quinoline and quinoline-hydriodide, gave only 2.5 per cent of methylenecyclohexane.¹⁸¹

4-Methylcyclohexene-1 (*i.e.*, 1-methylcyclohexene-3) was probably converted into "dimethylcyclopentene" when passed over silica gel at 450°, according to the insufficient evidence afforded by isolation of heptanes (b.p. 85.0-93.0°/741 mm. Hg, $D_4^{20}=0.6891$, $n_D^{20}=1.3900$) after the catalyzate was subjected to (a) hydrogenation, (b) dehydrogenation of methylcyclohexane, and (c) removal of toluene.⁶⁶⁵ This experiment also did not prove that dimethylcyclopentenenes were present in the catalyzate to the exclusion of 1-methyl-(2 or 3)-methylenecyclopentanes.

1-Methyl-4-isopropylcyclohexene-1 (*i.e.*, menthene-1 or carvomenthene) when passed as a vapor at 300-450° over bleaching earth, pumice, silica gel, the zeolite-like "tonsil," or a metal salt (such as magnesium sulfate or copper phosphate) yielded over 50 per cent of 1-isopropyl-4-methylcyclohexene-1 (*i.e.*, 1-methyl-4-isopropylcyclohexene-3; menthene-3 or menthomenthene):^{501, 521}



d-1-Methyl-4-isopropylcyclohexene-3 was partly racemized when boiled for 24 hours with alcohol containing *p*-toluenesulfonic acid.²⁵⁸

The reaction, however, can be used for the quantitative analysis of *d*-1-methyl-4-isopropylcyclohexene-2 and *d*-1-methyl-4-isopropylcyclohexene-3 mixtures, since the first hydrocarbon is much more slowly racemized.^{258a} Pending further investigations, the course of the main racemization can be considered as formation of the optically inactive ester of menthanol-4 and subsequent subtraction of *p*-toluenesulfonic acid.

d-1-Methyl-4-isopropylcyclohexene-3 formed "cyclopentene hydrocarbons" when passed twice over silica gel at 375°, 400°, or 450°. ⁶⁶⁶ "Cyclopentane hydrocarbons" were isolated after the catalyzates were subjected to (a) hydrogenation, (b) selective dehydrogenation, and (c) elimination of *p*-cymene. It was suggested that the isomers are di- or tri-substituted cyclopentenenes whose presence requires intermediary substituted bicyclohexanes. These experiments do not prove that "cyclopentene hydrocarbons" were present to the exclusion of (mono- or di-alkyl)-alkenyl cyclopentanes as isomers.

The isomerizations of cyclenes and cyclenes with saturated side-chains are given in Table 23, p. 318.

Conclusions

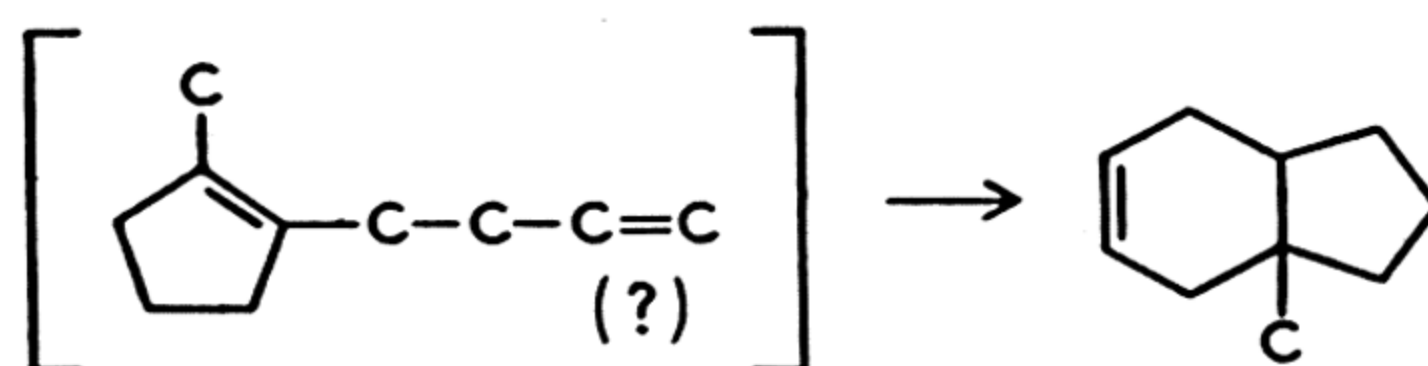
1. The double bond of cyclenes with saturated side-chains can shift into a new position in the ring and probably also into a side-chain.
2. The cyclopropene ring can be expected to decyclize, giving an alkadiene.
3. Cyclohexene rings probably form cyclopentenenes in some cases, possibly via alkadienes.

CYCLENES WITH UNSATURATED SIDE-CHAINS

Isomerizations

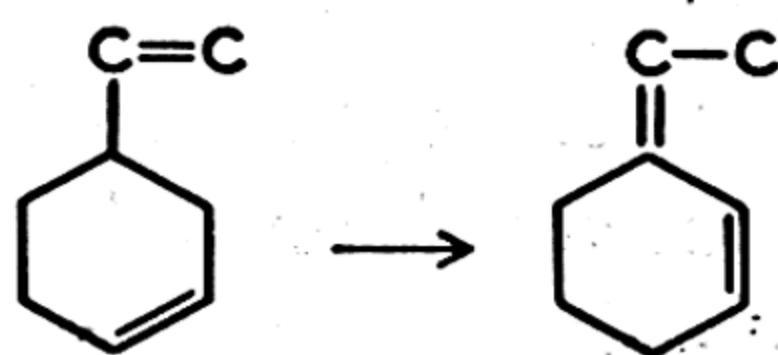
The cylenes with unsaturated side-chains belong to a hydrocarbon group wherein individual members have the ability to isomerize into several products. Their reactivity is chiefly due to the unsaturated side-chain, which can undergo shifts of the double bond or can cause further cyclization into bicyclic hydrocarbons.

Treatment of 1-methyl-2-(3-butenyl)cyclopentene-(1?) with phosphoric acid plus phosphorus pentoxide resulted largely in a cyclization to 3a-methyl-3a,4,7,7a-tetrahydroindan:¹⁷⁰



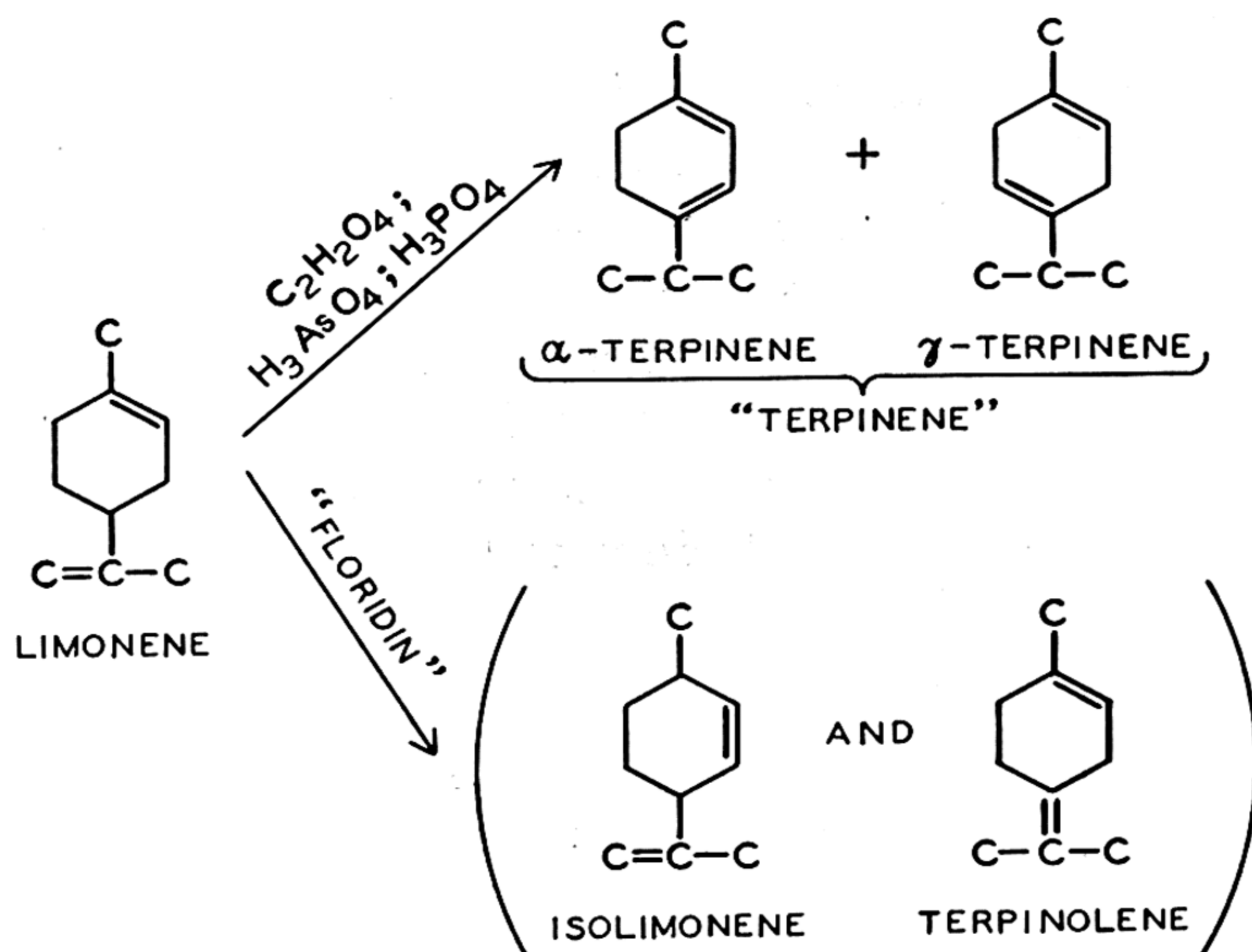
Probable Structure¹⁷⁰

1-Vinylcyclohexene-3 isomerized to 1-ethylidenecyclohexene-2 at 200-235° in the presence of "Floridin."⁵⁵⁰ In this reaction, both double bonds move to form a conjugated system:



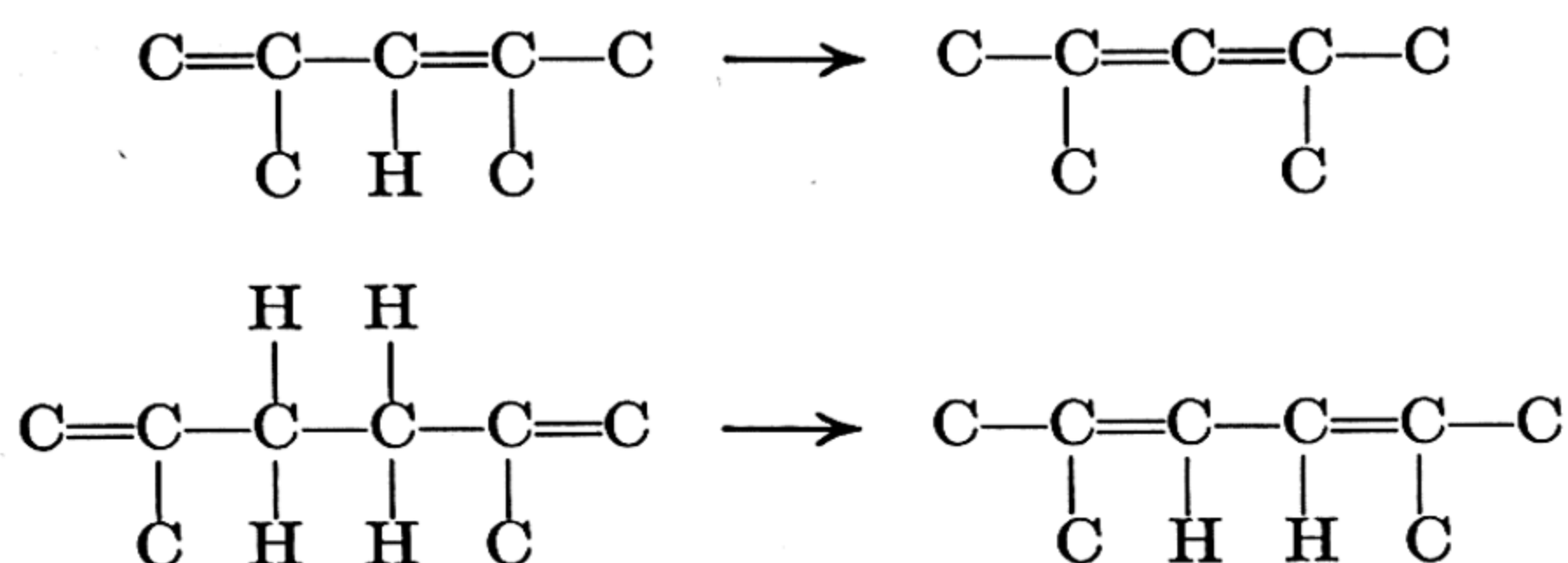
Optically active 1-methyl-4-isopropenylcyclohexene-1 ("limonene" by definition) is "inverted" or racemized to dipentene (*dl*-limonene) when heated several hours at 250-270°^{108, 615} or at 380°.¹⁰⁸ There are no effective catalysts for the racemization of limonene.¹⁰⁷

d-Limonene formed a little α - and γ -terpinenes and much diterpene when treated with phosphoric acid at 22-32°;¹⁰³ α -terpinene was reported as the only isomer on heating limonene with anhydrous oxalic acid.³⁹⁴ Limonene when heated under reflux with arsenic acid gave "terpinene,"^{208, 209} but when passed over hot "Floridin," yielded 1-methyl-4-isopropenylcyclohexene-2 (isolimonene) and probably some 1-methyl-4-isopropylidenecyclohexene-1 (terpinolene).⁵⁵⁰ There was no 1-methyl-4-isopropylidenecyclohexene-2 (isoterpinolene) among the products, probably due to its removal by polymerization. Dipentene, which is *dl*-limonene, was changed into "terpinene" and a polymer called "dipinene," when heated under reflux with fuller's earth for 1.5 hours.⁶¹⁰ Dipentene yielded considerably over 26 per cent of terpinolene and 12.9 per cent of polymers when heated at 170° for one hour with 0.5 per cent of activated Chasov-Jarsky clay.^{480a} Further treatment of the product (polymer-freed and containing over 53 per cent of dipentene) for an hour with one per cent of the same catalyst resulted in the formation of 15.8

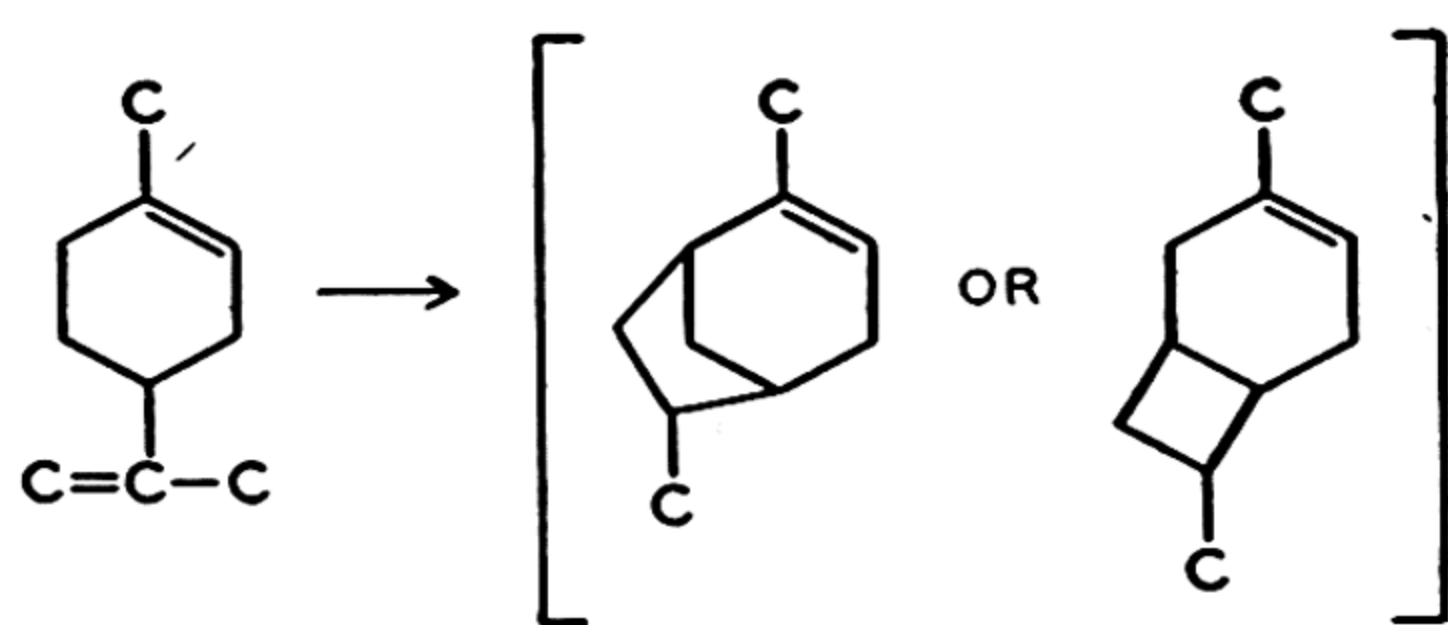


per cent of α -terpinene, presumably at the expense of part of the terpinolene. Four consecutive treatments of dipentene with the activated clay, however, led to the formation of menthene-3 and *p*-cymene, as terpene disproportionation products, and to much polymer.

It is of interest to note that in the isomerization to terpinolene, and possibly (transitionally) in the formation of "terpinene," the isopropenyl group of limonene becomes an isopropylidene group. This change is similar to the following aliphatic three-carbon isomerizations involving isopropenyl groups:

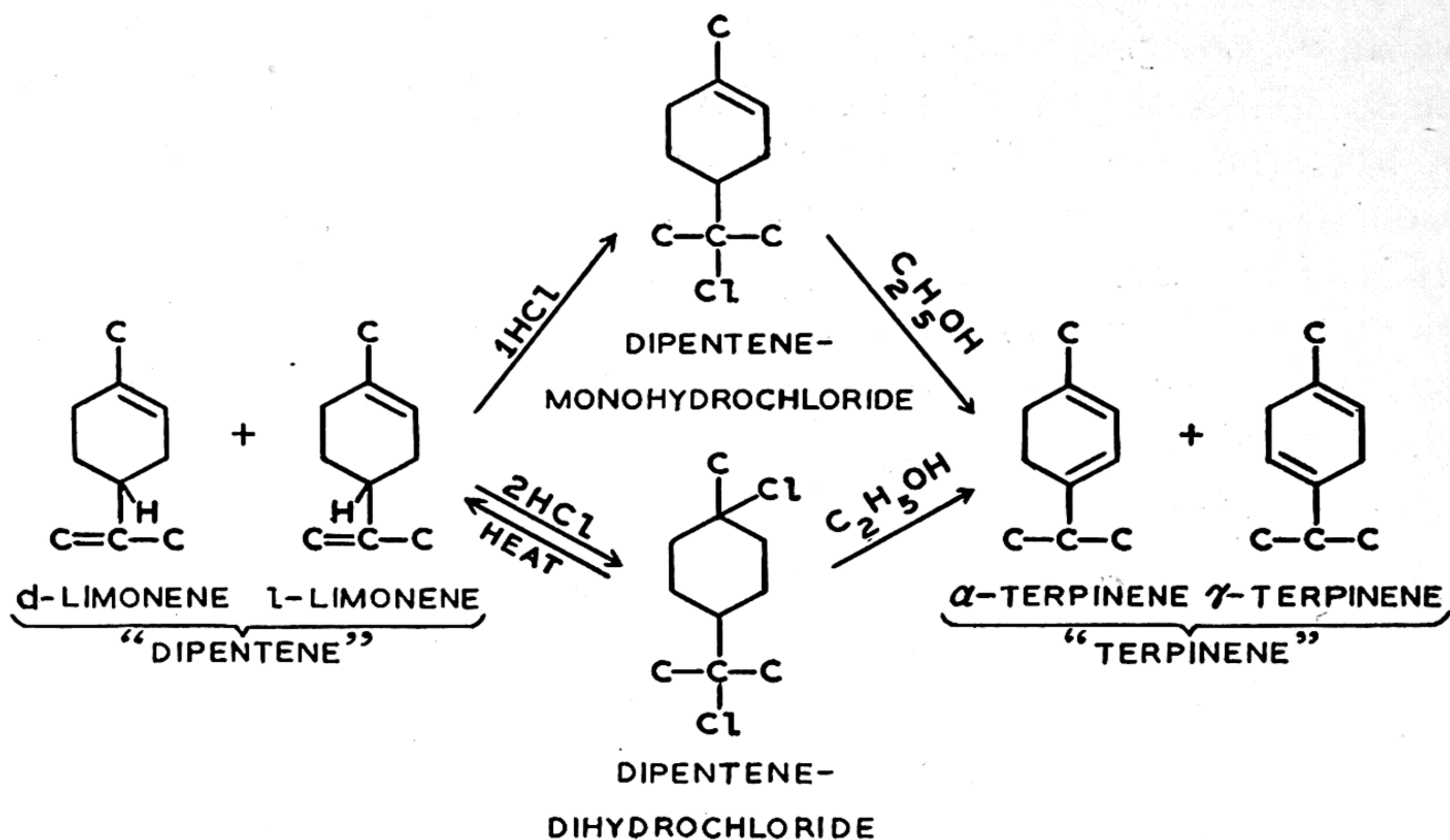


The isopropenyl group of limonene can also enter into cyclizations, yielding two isomeric bicyclic terpenes.^{275a} The required conditions are passage of the limonene over a phosphoric acid on silica catalyst at 150-250°. The resulting isomers (b.p. 163-165°/750 mm. Hg, $D_4^{19} = 0.8416$, $n_D^{20} = 1.4630$; b.p. 169-171°/750 mm. Hg, $D_4^{20} = 0.8444$, $n_D^{20} = 1.4674$) are believed to be *cis* and *trans* forms of 2,6-dimethylbicyclo[3.2.1]octene-2, or possibly of 3,7-dimethylbicyclo[4.2.0]octene-3:

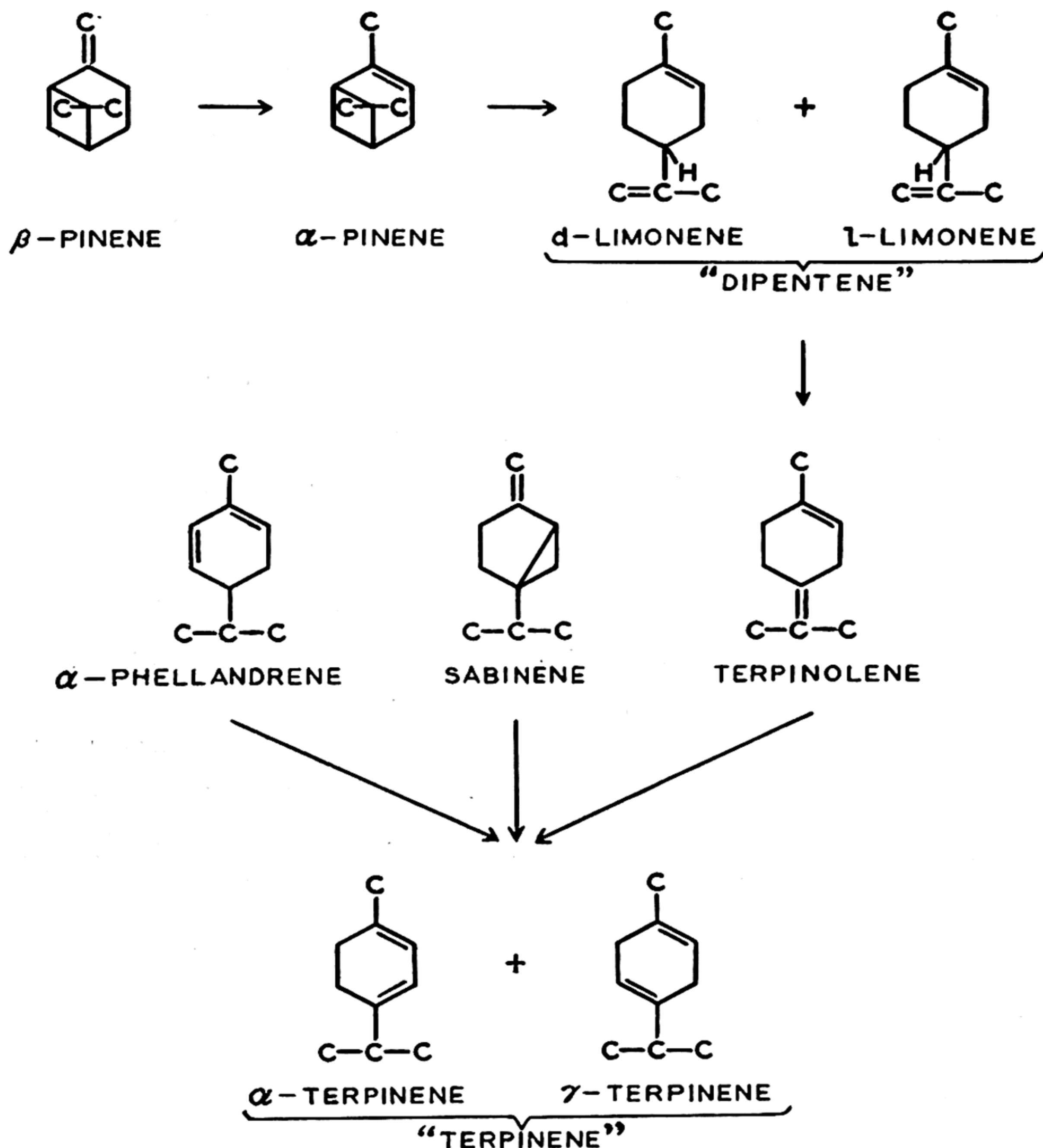


Hydrogenation of the two isomers under pressure in the presence of a nickel-kieselguhr catalyst yielded a bicyclane (b.p. 170.5/750 mm. Hg, $D_4^{27} = 0.8283$, $n_D^{20} = 1.4530$).

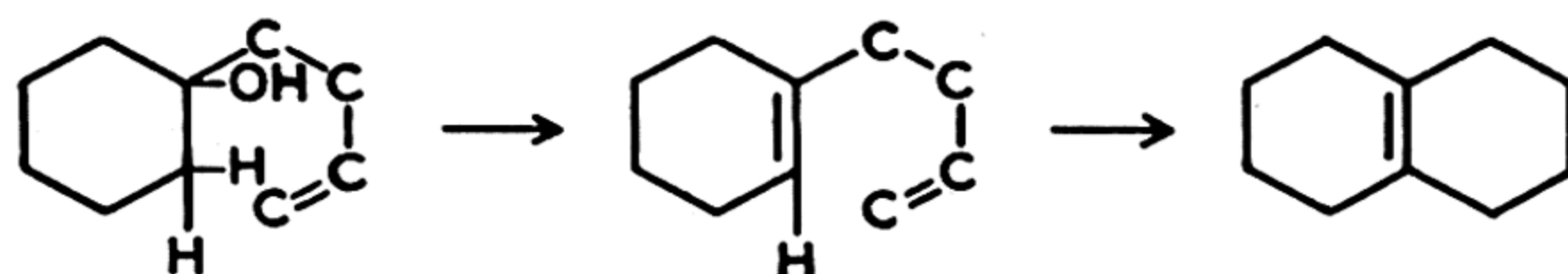
Dipentene (*dl*-limonene), treated for 1 hour with alcoholic sulfuric acid at 100°, formed "terpinene" and much resin.⁶¹⁷ Alcoholic hydrochloric acid is probably a catalyst also, since dipentene-dihydrochloride gave "terpinene" when heated under reflux for 3 hours with alcohol.⁶¹⁷ Dipentene-dihydrochloride heated for 3 hours under reflux, then steam-distilled, yielded a principal fraction containing dipentene;⁶¹⁶ this indicates an equilibrium state. Dipentene-monohydrochloride is an intermediate in the formation of "terpinene."^{617, 618}



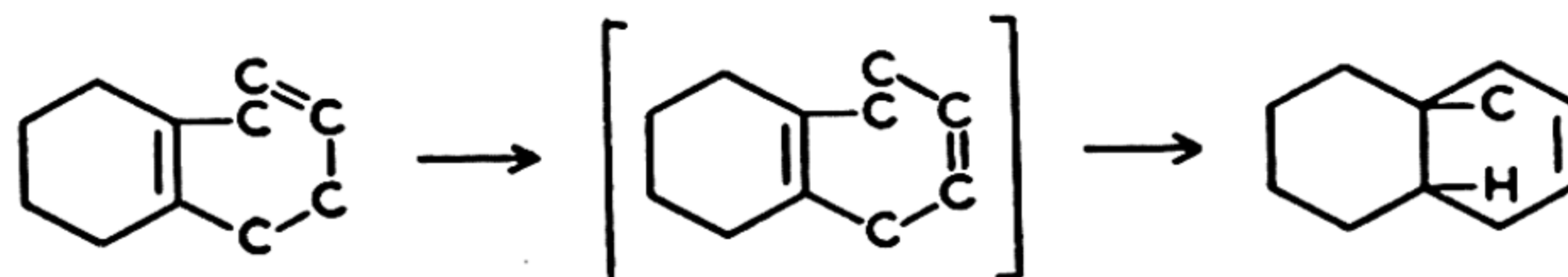
Terpinolene heated with acids gives "terpinene."⁶²⁰ This isomerization is of considerable theoretical significance in terpene chemistry. The probable courses of terpene isomerizations yielding "terpinene" are:



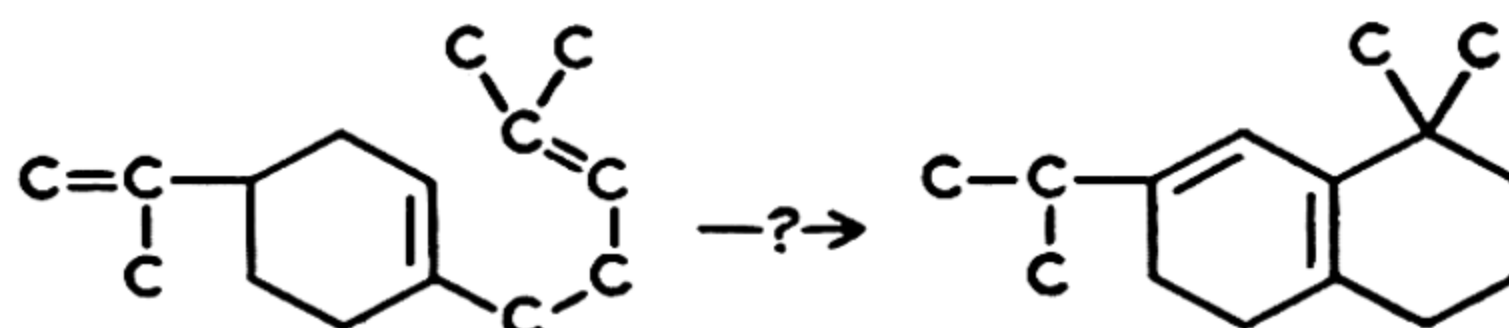
A mixture of 1-(3-butenyl)cyclohexene-1 and 1,2,3,4,5,6,7,8-octahydronaphthalene ($\Delta^{9,10}$ -octalin) resulted when 1-(3-butenyl)cyclohexanol-1 was heated under reflux for 3 hours at 160° with phosphoric acid plus phosphorus pentoxide. The cyclization of the diene was completed by treatment of the hydrocarbon mixture with phosphorus pentoxide (30 per cent) for 3 hours at 140° .³⁵³ This cyclization is analogous to the intermolecular dimerization of an alkene:



1-Methyl-2-(3-butenyl)cyclohexene-1, in the presence of phosphoric acid at 130° , formed *cis*-9-methyl-1,4,5,6,7,8,9,10-octahydronaphthalene.²⁵³ The cyclization can be explained by assuming the formation of an intermediate, such as 1-methyl-2-(2-butenyl)cyclohexene-1:

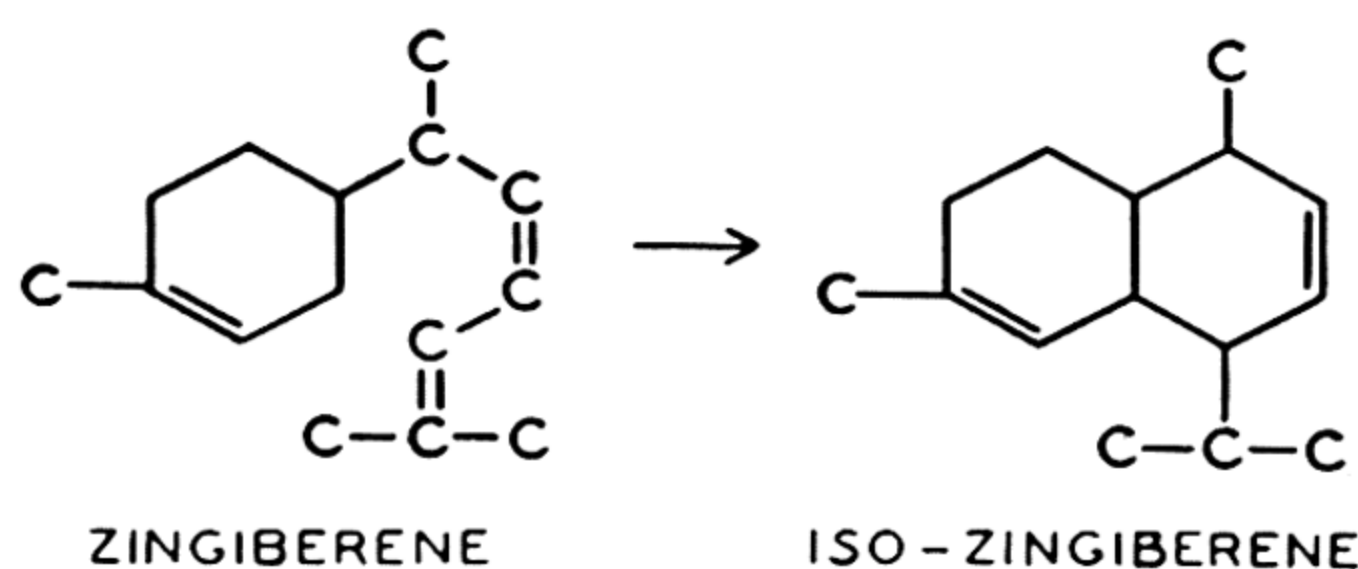


Cycloisoprenemyrcene, when heated at 100° for 10 hours and then at 120° for 2 hours with 85-per cent formic acid, was converted into 66.7 per cent of bicycloisoprenemyrcene.⁴⁸⁴ This isomerization has been formulated tentatively as follows:⁴⁸⁴

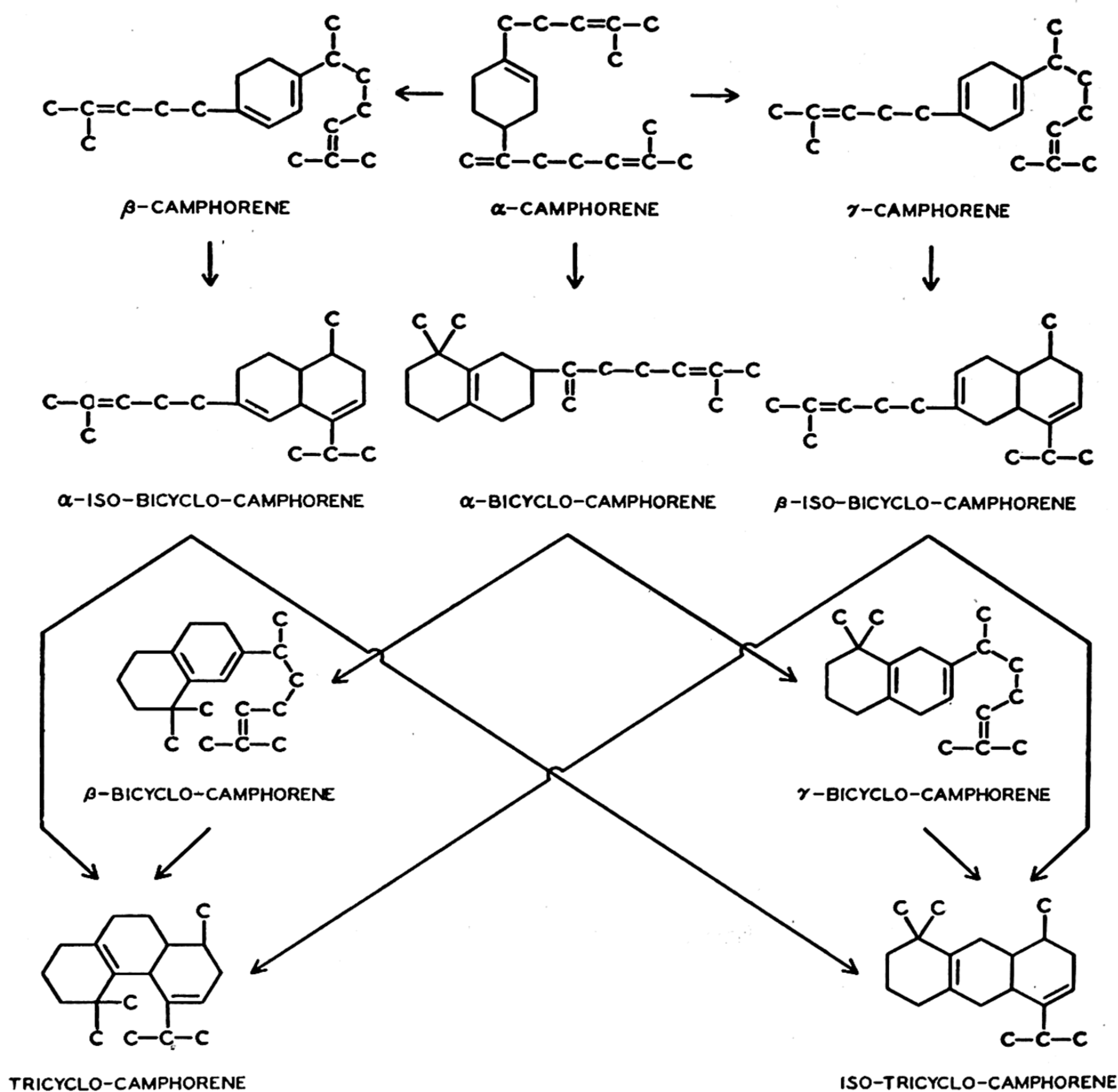


If one adopts Ruzicka and Stoll's system of nomenclature for the camphorenes,⁴⁹⁴ then the above cyclization should be considered as that of α -cycloisoprenemyrcene into β -bicyclo-isoprenemyrcene.

l-Zingiberene, which is another monocyclic sesquiterpene, formed the bicyclic *l*-iso-zingiberene when treated for 6 hours at 60 – 65° with acetic acid containing diluted sulfuric acid.^{490, 495, 535} Since the structure of zingiberene is established, whereas that of iso-zingiberene is deducible from the product (cadalene) obtained in its dehydrogenation,⁴⁹⁰ the cyclization may be formulated as follows:

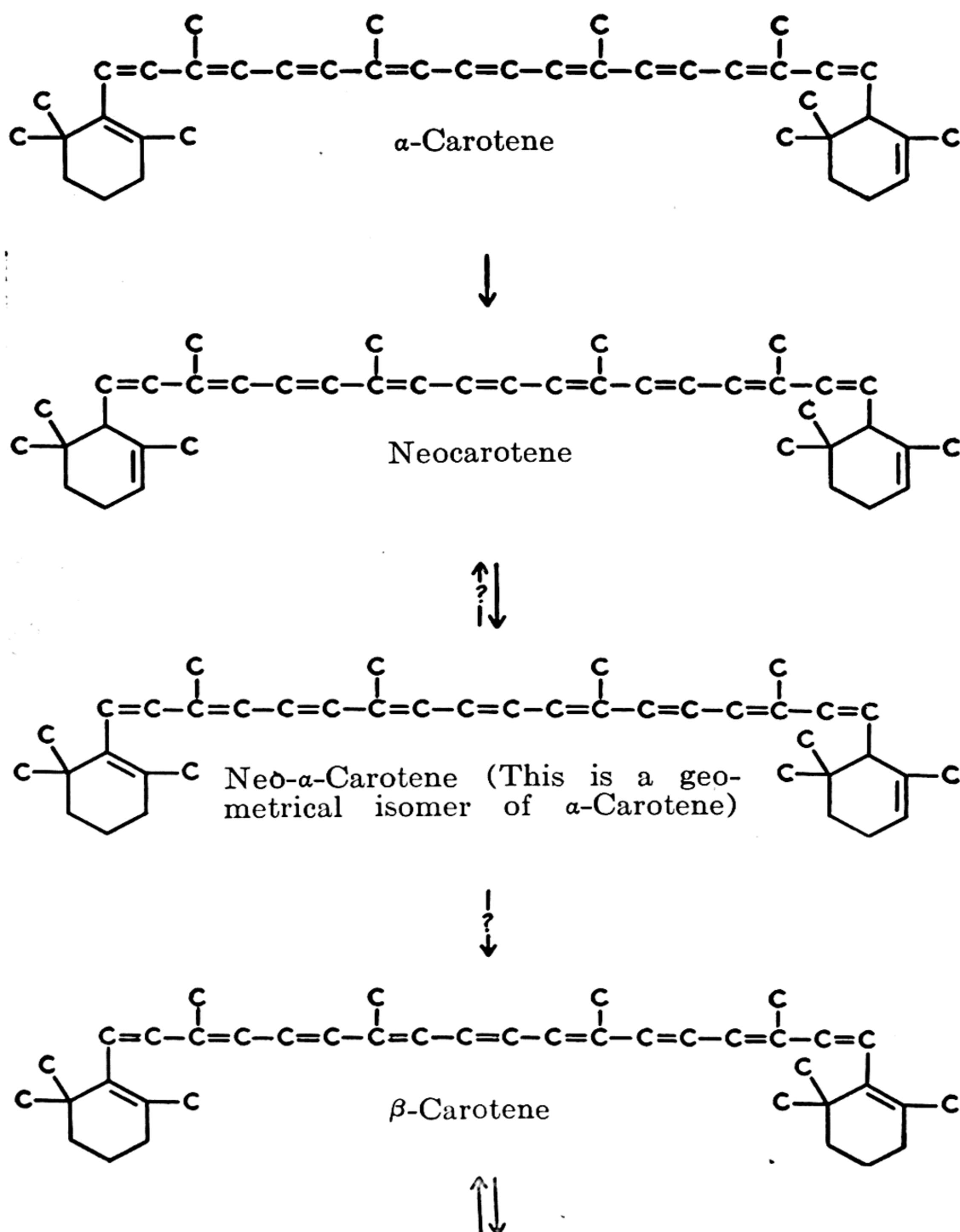


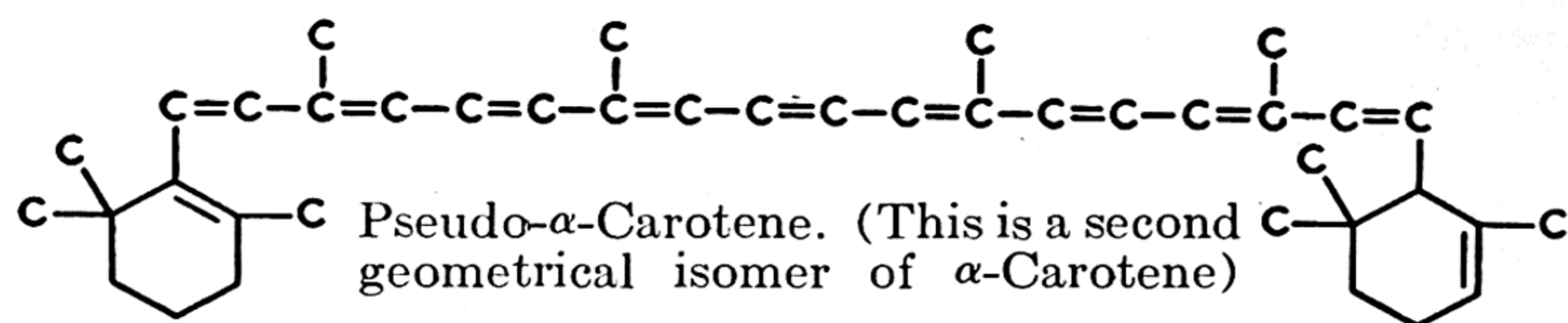
α -Camphorene, which is a monocyclic diterpene as well as the dimer of myrcene, gives a bicyclic isomer when heated (0.5 hour) with 95-per cent formic acid, but forms a tricyclic isomer upon a further 3 hours' heating with the acid.⁴⁹⁴ This bicyclic isomer was produced previously by treatment of α -camphorene with acetic acid containing sulfuric acid;⁵³⁷ unfortunately,⁴⁹⁴ it was called "iso- α -camphorene." The structural formula of α -camphorene is established definitely, but formulas of the bicyclic and tricyclic isomers are not settled. Some of the possible structures⁴⁹⁴ that can be assigned to these isomers are presented in the following group of α -camphorene isomerizations:



1-(2,6,6-Trimethylcyclohex-1-en-1-yl)-3,7,12,16-tetramethyl-18-(2,6,6-trimethylcyclohex-2-en-1-yl)-octadecanonaene-1,3,5,7,9,11,13,15,17 (*i.e.*, pseudo- α -carotene) has been converted into 1,18-bis-(2,6,6-trimethylcyclohex-1-en-1-yl)-3,7,12,16-tetramethyl-octadecanonaene-1,3,5,7,9,11,13,15,17 (*i.e.*, β -carotene), and vice versa. The processes used are:

chromatographic or differential adsorption on alumina,²¹⁰ addition of iodine to benzene solutions,⁶⁶¹ and aging of solutions made up with light petroleum and benzene.¹⁰² These isomerizations involve the shift of only one double bond (in a ring), out of a total of 11 double bonds in the molecule. α -Carotene, which is a geometrical isomer of pseudo- α -carotene²¹⁰ and of neo- α -carotene,²¹¹ has been reported to isomerize into neocarotene by treatment with magnesium oxide²¹⁰ or alumina.^{210, 211} Neocarotene is probably a *structural* isomer with 9 conjugated double bonds.²¹⁰ It is converted into neo- α -carotene upon mere crystallization.²¹¹ Neo- α -carotene subjected to adsorption on alumina probably yields β -carotene and neocarotene. These several isomerizations can be considered as interconversions of 5 related deoctahydro-tetraterpenes or carotenoids:





Pseudo- α -carotene has been found among the oxidation products of β -carotene with dilute potassium permanganate solution, as determined by subsequent chromatographic adsorption on calcium hydroxide.^{296, 297} The carotenes are hydrocarbon members of an important and interesting group (carotenoids) of polyene pigments present throughout the plant and animal kingdom.^{71aa, 71b, 71c}

1-Ethynylcyclohexene-1, passed with carbon dioxide over platinum-charcoal at 200-205°, was isomerized completely into ethylbenzene:³⁴⁴



This remarkable reaction indicates that aromatizations of cyclohexenes into valuable aromatics can be expected to occur by isomerization alone whenever alkynyl groups are present in the molecule. The mechanism involves a transfer of 4 hydrogen atoms from the ring to the side-chain, and a stabilization of the molecule through resonance effects.

Isomerizations of cyclenes with unsaturated side-chains are listed in Table 24, p. 322.

Conclusions

1. Cyclenes with unsaturated side-chains undergo isomerization by: (a) shifts of double bonds present in the ring or side-chain, and (b) cyclization into bicyclic or tricyclic isomers.

2. Catalysts of mild activity, such as alumina, "Floridin," and magnesia, may effect an isomerization by the shift of only one double bond, even though as many as 11 double bonds are present in the molecule.

3. Acids cause cyclization and a shift of side-chain double bonds into the rings newly formed or already present.

4. A cyclohexene with an alkynyl side-chain gives an aromatic in the presence of platinum-charcoal (a useful isomerization).

CYCLODIENES WITH SATURATED SIDE-CHAINS

Isomerizations

Only a few examples of isomerization are available in the group of cyclodienes (monocyclodiolefins) with saturated side-chains. 1-Methyl-

4-isopropylcyclohexadiene-1,3 (*i.e.*, α -terpinene), treated with phosphoric acid for 200 hours at room temperature, remains unisomerized and can be recovered unchanged.¹⁰³ This behavior is expected on account of easy formation from its isomers, the terpenes, and its symmetrical structure (see page 130).

1-Methyl-4-isopropylcyclohexadiene-1,4 (*i.e.*, γ -terpinene) is believed to undergo an isomerization to 1-methyl-4-isopropylcyclohexadiene-1,3 (*i.e.*, α -terpinene) when treated with acidic reagents.^{206b} Nine per cent of α -terpinene-maleic anhydride adduct was formed when γ -terpinene and maleic anhydride were heated together^{206b} in the customary manner.^{206a}

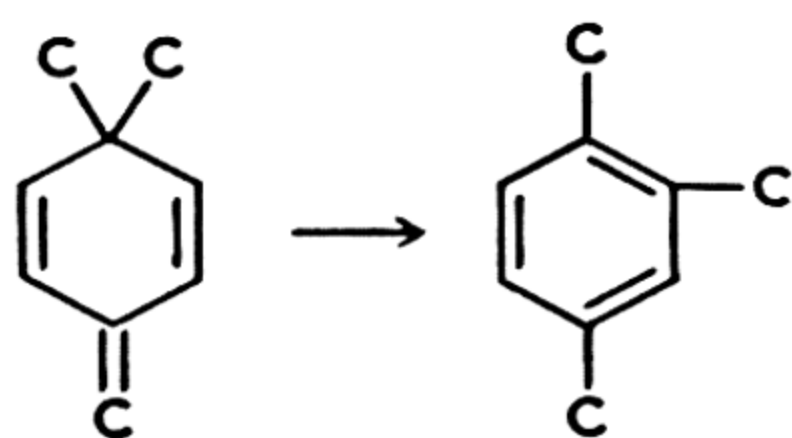
l-1-Methyl-4-isopropylcyclohexadiene-1,5 (*i.e.*, *l*- α -phellandrene) isomerized into α - and γ -terpinenes under the catalytic action of phosphoric acid.¹⁰³ This reaction was accompanied by the formation of polymers. When heated for several hours under reflux with alcoholic sulfuric acid, a preparation rich in α -phellandrene gave resins and a volatile fraction containing "terpinene."⁶¹⁷ Mere shaking of *d*- α -phellandrene with alcoholic sulfuric acid for a few minutes also gives "terpinene."⁶¹⁹

The isomerizations of α -terpinene and α -phellandrene in the presence of catalysts are listed in Table 25, p. 328.

CYCLODIENES WITH UNSATURATED SIDE-CHAINS

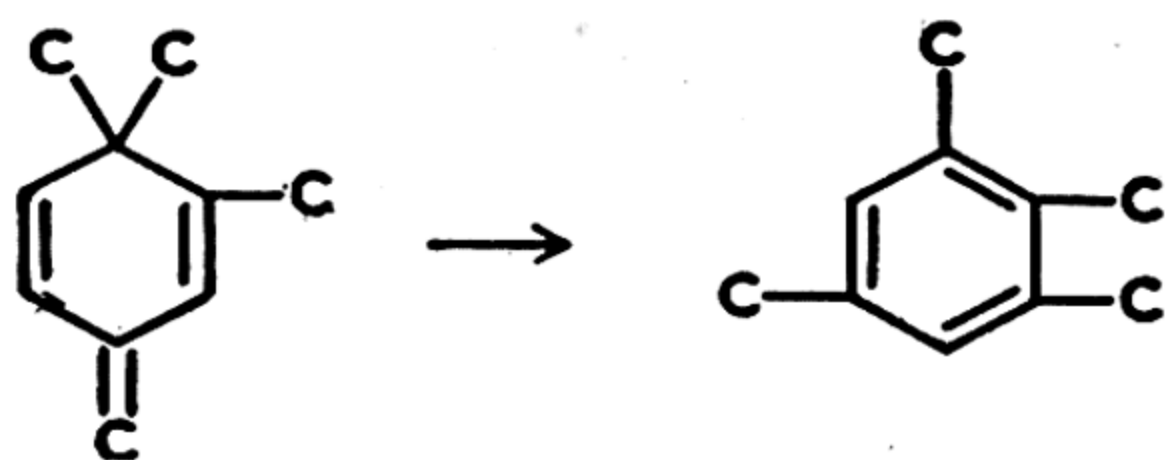
Isomerizations

The cyclodienes containing a six-carbon ring and 3 double bonds per molecule can isomerize irreversibly to a system of 3 conjugated double bonds (aromatics). This has been accomplished by the catalytic action of hydrochloric or sulfuric acid on cyclodiene hydrocarbons of the "semi-benzene" type (acetic acid solutions).²³ 1,1-Dimethyl-4-methylenecyclohexadiene-2,5, the simplest semi-benzene known, isomerized into 1,2,4-trimethylbenzene (pseudocumene), within one hour at 0° in acetic acid solution saturated with hydrogen chloride.²³ The same reaction occurred probably spontaneously when 1,1-dimethyl-4-methylenecyclohexadiene-2,5 was heated alone to about 160° at atmospheric pressure:²²

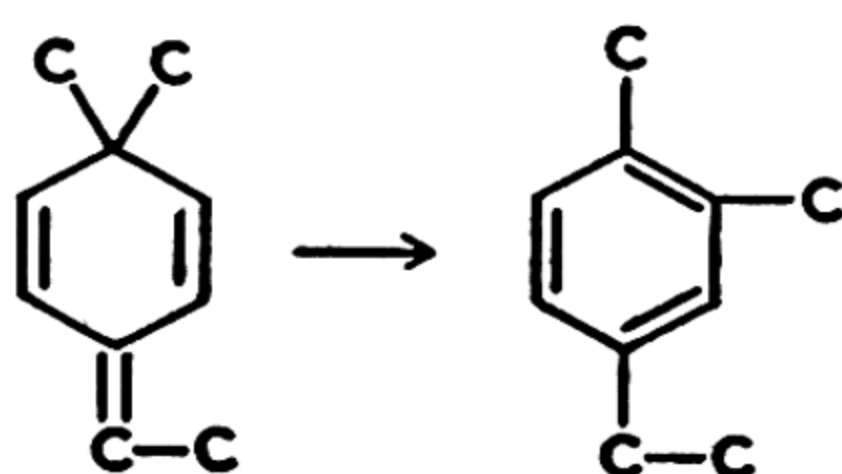


1,1,2-Trimethyl-4-methylenecyclohexadiene-2,5, treated in acetic acid solution with sulfuric acid, probably formed a small amount of 1,2,3,5-

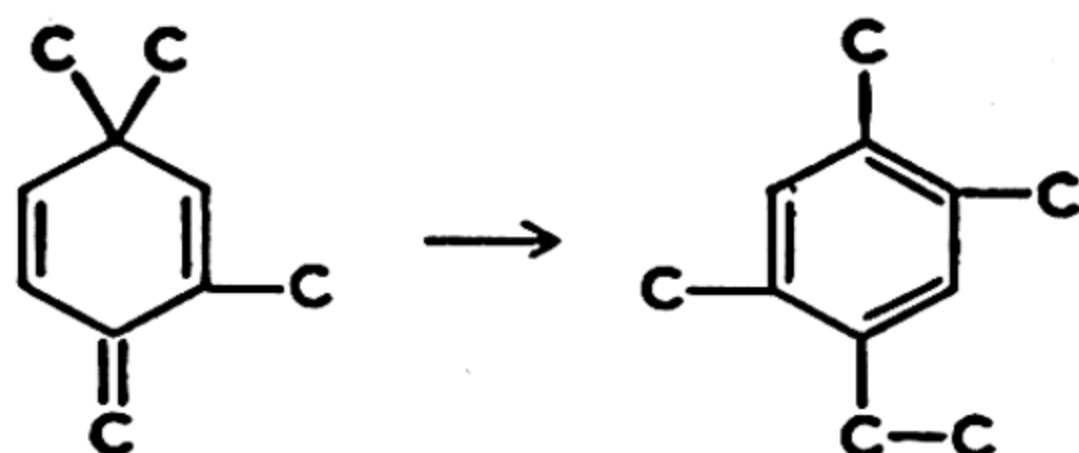
tetramethylbenzene (isodurene), and a large amount of a polymerization product:²³



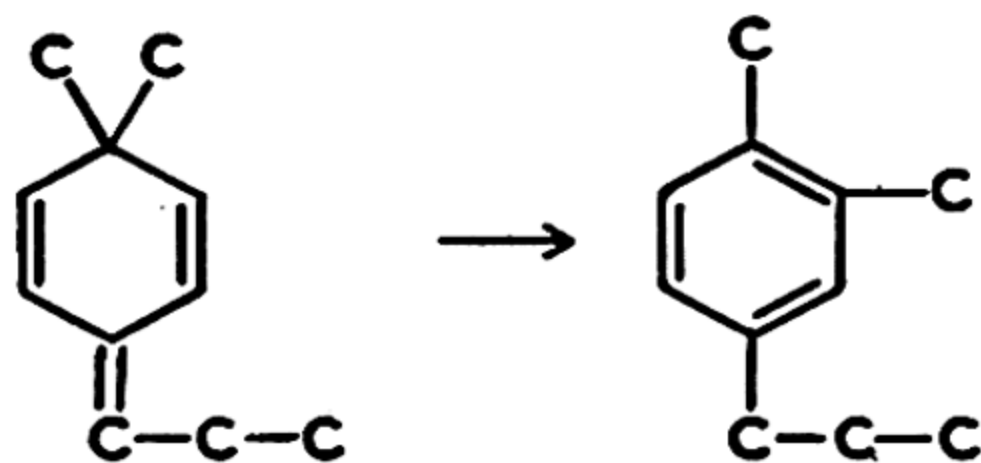
1,1-Dimethyl-4-ethylidenecyclohexadiene-2,5, in acetic acid, formed 1,2-dimethyl-4-ethylbenzene when treated with hydrochloric acid:²³



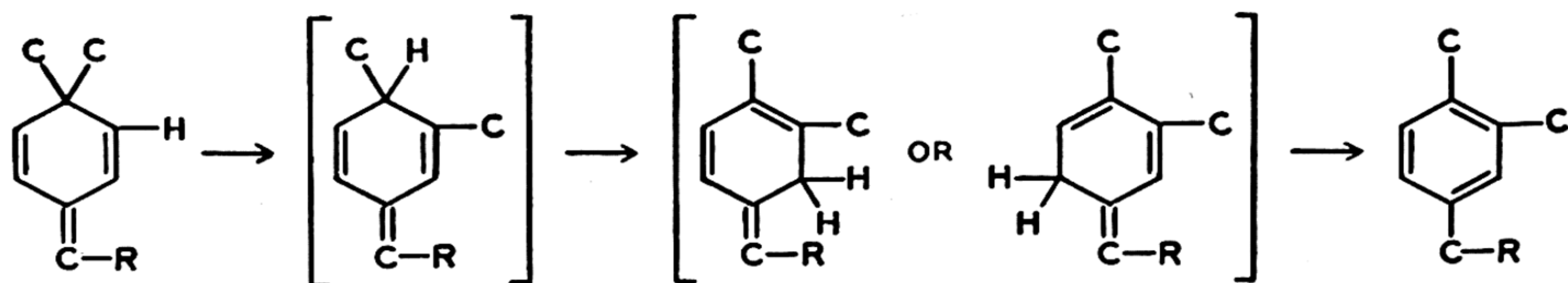
1,1,3-Trimethyl-4-ethylidenecyclohexadiene-2,5 (in acetic acid) gave 1,2,5-trimethyl-4-ethylbenzene (*i.e.*, sym-ethyl-pseudocumene) upon the addition of 70-per cent sulfuric acid.²³ The reaction is exothermic, and the temperature of the mixture changed from 20° to a final 40°:



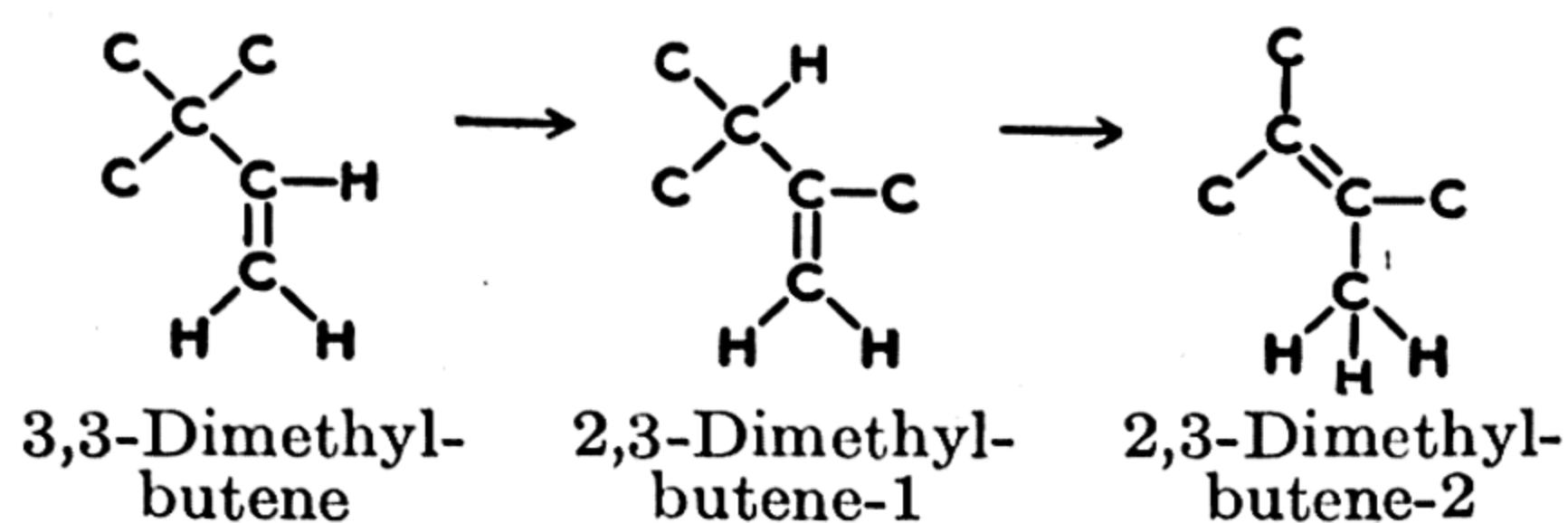
1,1-Dimethyl-4-propylidenecyclohexadiene-2,5, in acetic acid solution containing a little hydrochloric acid, gave 1,2-dimethyl-4-propylbenzene:²³



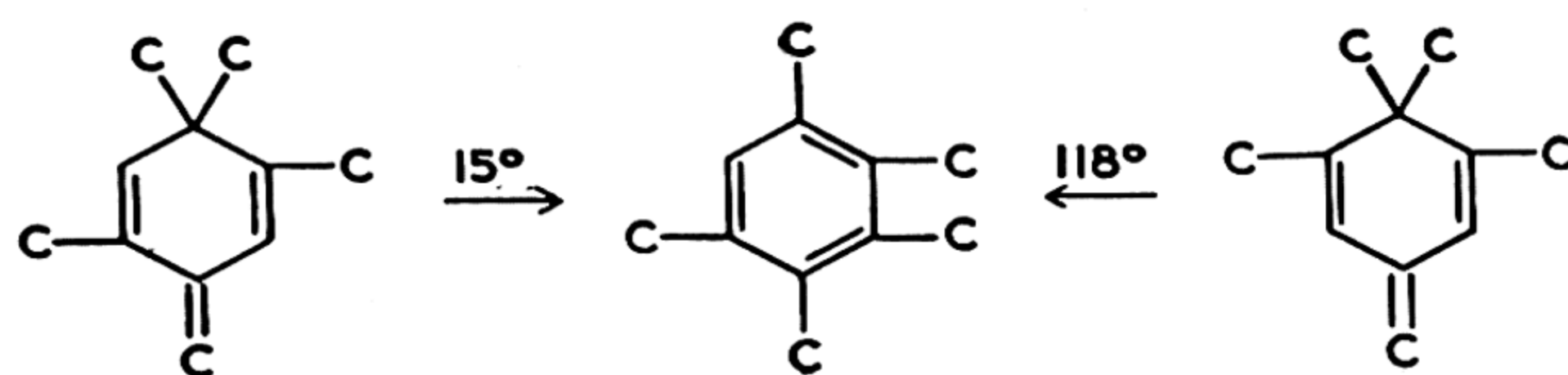
The five preceding instances of isomerization are of the following type:



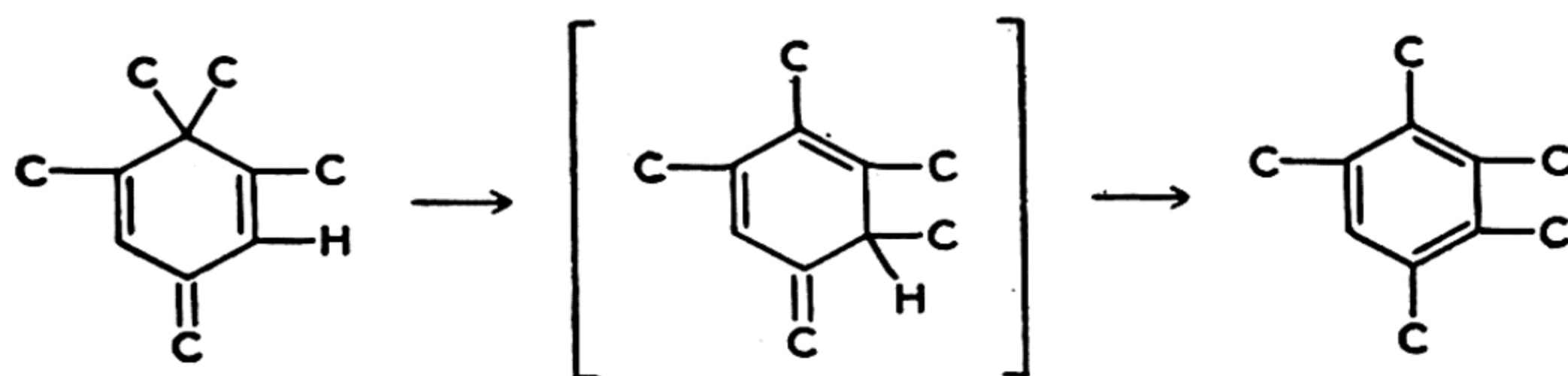
They correspond to the formations of 2,3-dimethylbutene-2 from 3,3-dimethylbutene (via 2,3-dimethylbutene-1) and of α -terpinene from terpinolene:



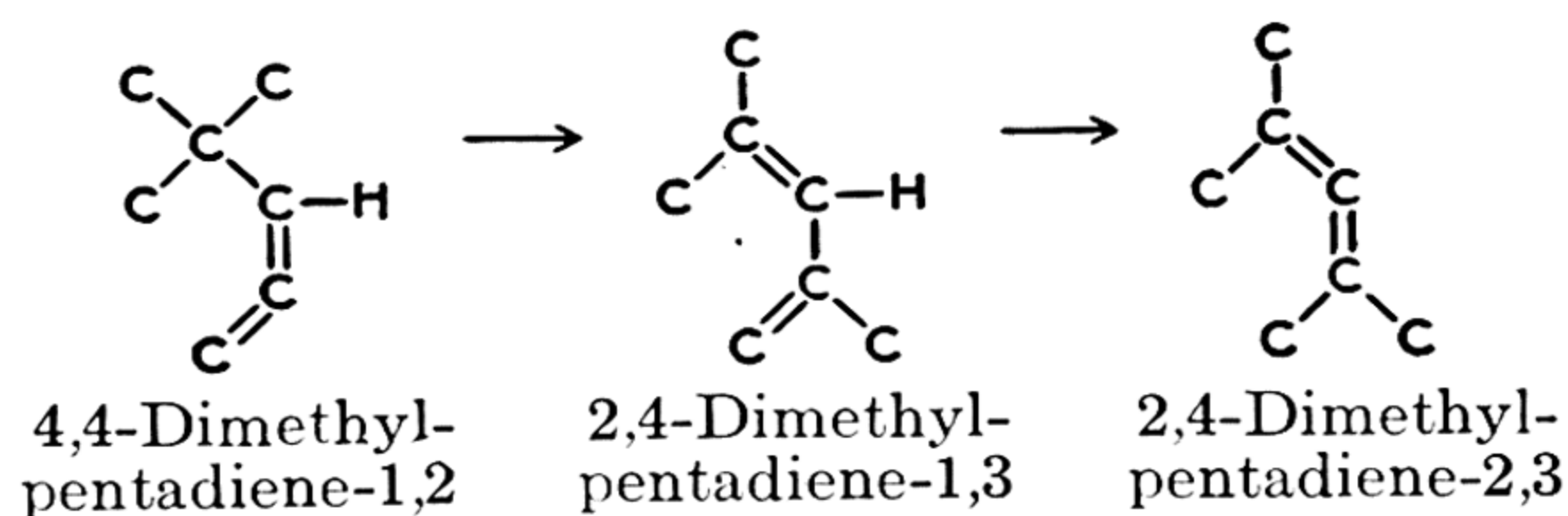
1,1,2,5- and 1,1,2,6-Tetramethyl-4-methylenecyclohexadienes-2,5 (in acetic acid) yielded pentamethylbenzene when treated with hydrochloric and sulfuric acids, respectively.²³ The first hydrocarbon reacted rapidly with development of heat (temperature range, 15° to 30°), whereas the second hydrocarbon required *heating* to the boiling point:



The isomerization of 1,1,2,6-tetramethyl-4-methylenecyclohexadiene-2,5 into pentamethylbenzene is similar to that of 4,4-dimethylpentadiene-1,2 into 2,4-dimethylpentadiene-2,3. The isomerization of 1,1,2,6-tetramethyl-4-methylenecyclohexadiene-2,5 probably involves a preliminary alkyl and unsaturated-bond shift without hydrogen transfer, since the corresponding initial isomerization of 4,4-dimethylpentadiene-1,2 into 2,4-dimethylpentadiene-1,3 occurs without hydrogen transfer:

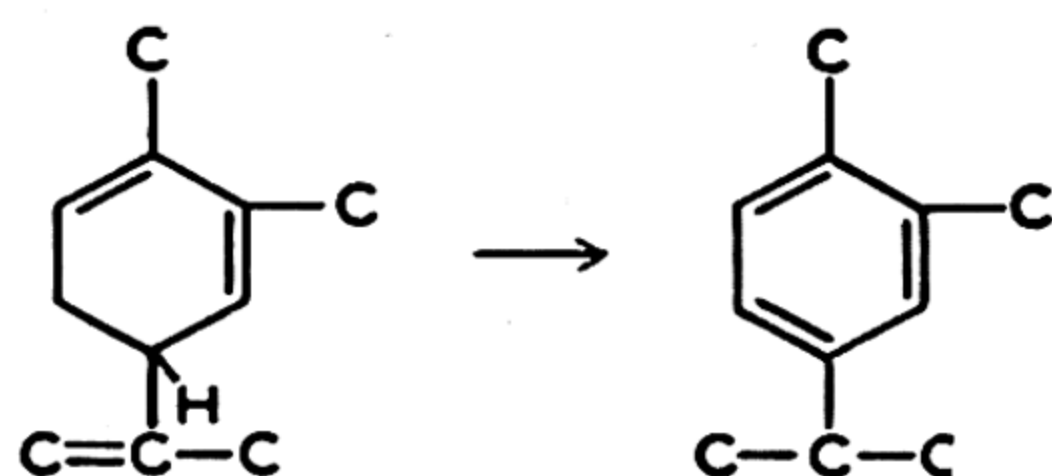


which corresponds to the isomerizations:

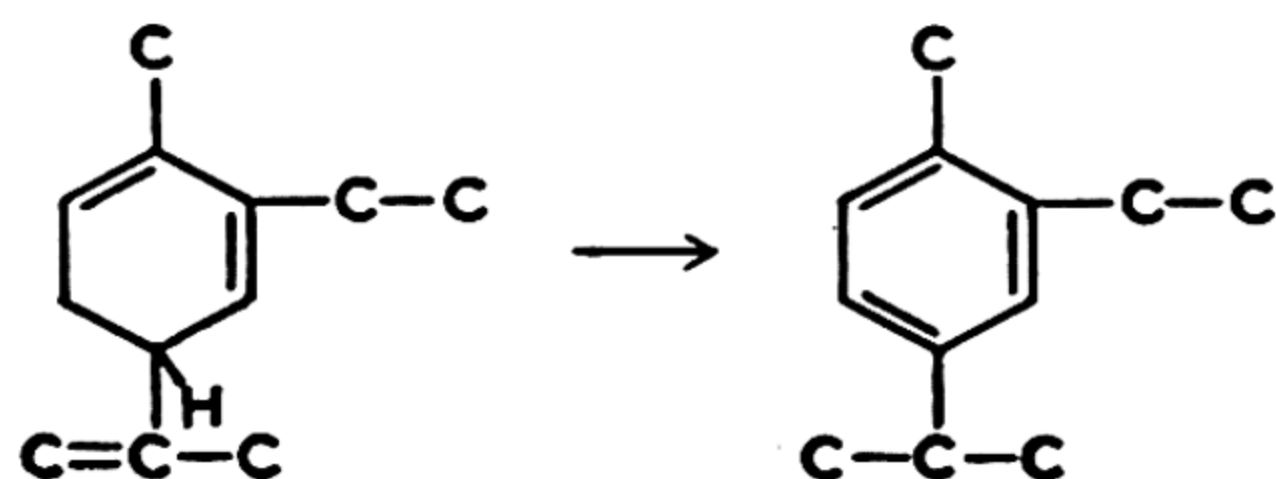


These isomerizations are completed by a prototropic three-carbon, or "terpinolene \rightarrow α -terpinene," change.

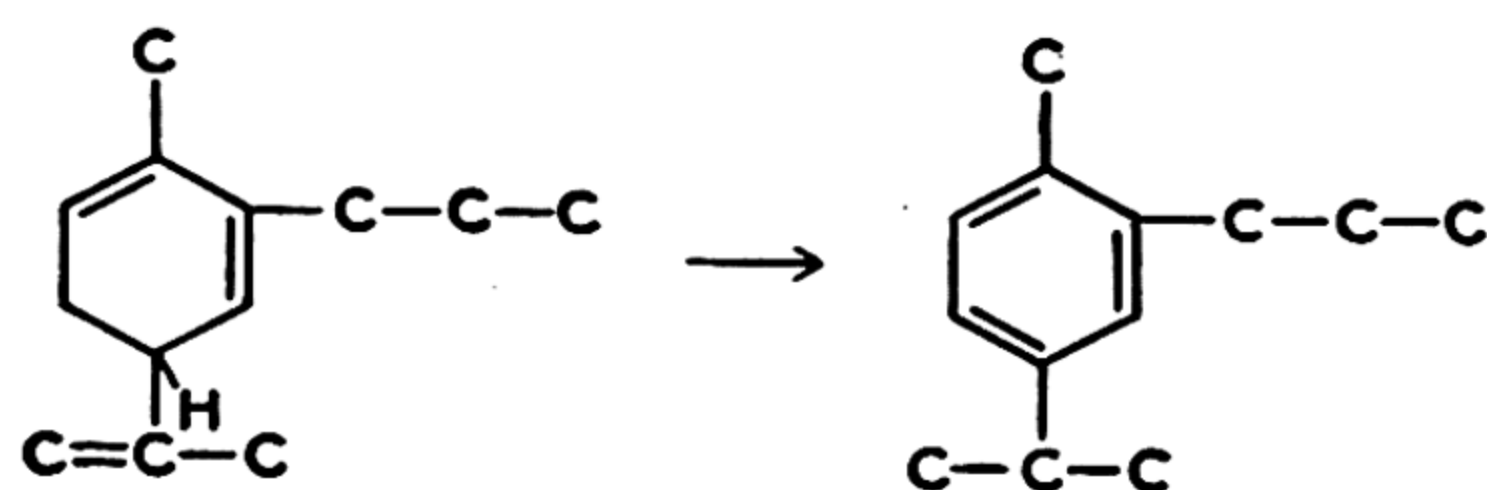
d-1,2-Dimethyl-4-isopropenylcyclohexadiene-2,6 was heated under reflux for 5 hours with 2-per cent hydrogen chloride in acetic acid, forming 70 per cent of 1-2-dimethyl-4-isopropylbenzene:³¹¹



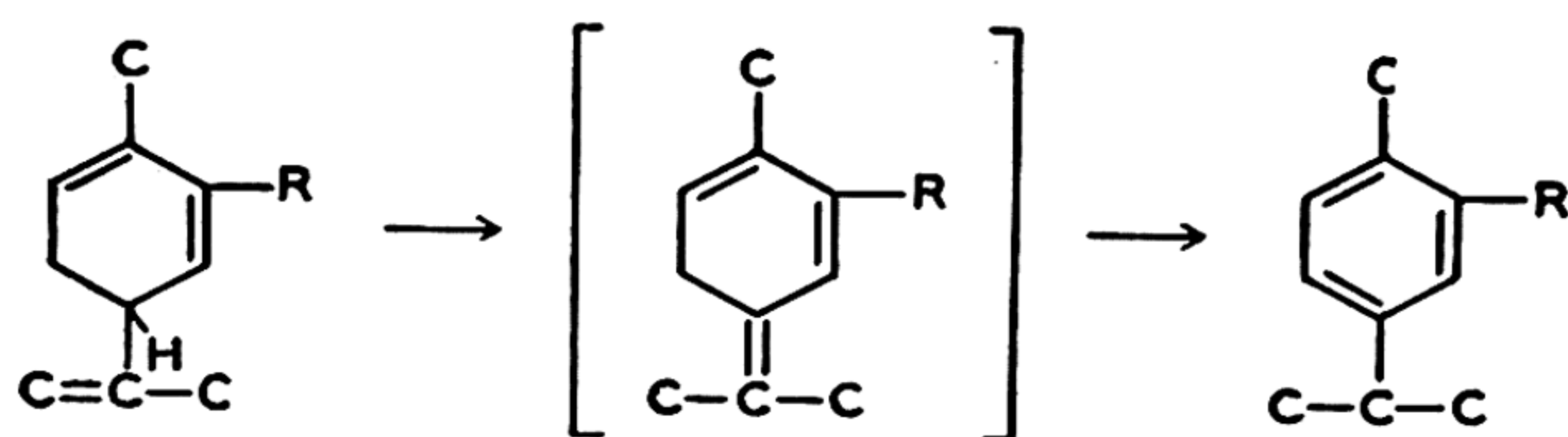
d-1-Methyl-2-ethyl-4-isopropenylcyclohexadiene-2,6, heated under reflux for 5 hours with 2-per cent hydrogen chloride in acetic acid, formed 1-methyl-2-ethyl-4-isopropylbenzene:³¹¹



d-1-Methyl-2-propyl-4-isopropenylcyclohexadiene-2,6, treated for 4 hours with 3-per cent hydrogen chloride in acetic acid, gave 60 per cent of 1-methyl-2-propyl-4-isopropylbenzene:³¹⁰



The three preceding isomerizations correspond to the stepwise formation of terpinolene and α -terpinene from limonene; they are examples of a simple type of aromatization by hydrogen migration:



l- β -Curcumene is a monocyclic-sesquiterpene mixture containing 1-methyl-4-(1,5-dimethylhex-4-en-1-yl)-cyclohexadiene-1,4 and 1-methyl-4-(1,5-dimethylhex-5-en-1-yl)-cyclohexadiene-1,4.¹⁰¹ It underwent isomerization to isomers of unknown structure when (a) heated at 380° in an inert atmosphere under pressure, or (b) treated with sodium plus amyl alcohol, or (c) subjected to 10-per cent sulfuric acid for several hours.⁴⁵⁹ The last reagent gave a levorotatory bicyclic sesquiterpene.

Isomerizations of cyclodienes with unsaturated side-chains are given in Table 26, p. 328.

Conclusions

1. The conversion of alkenyl-polyalkyl cyclohexadienes-2,6 into poly-

alkyl benzenes (by acids) is one of the simpler forms of isomerization by "aromatization."

2. The isomerization of alkylidene-polyalkyl cyclohexadienes-2,5 into polyalkyl benzenes (by acids) is a less simple aromatization because of an additional step, namely, conversion into intermediary alkylidene-polyalkyl cyclohexadienes-1,5 (or -2,6).

3. The isomerization of 1,1,2,6-tetramethyl-4-methylenecyclohexadiene-2,5 into pentamethylbenzene is an example of a complex aromatization whose mechanism is nevertheless understood.

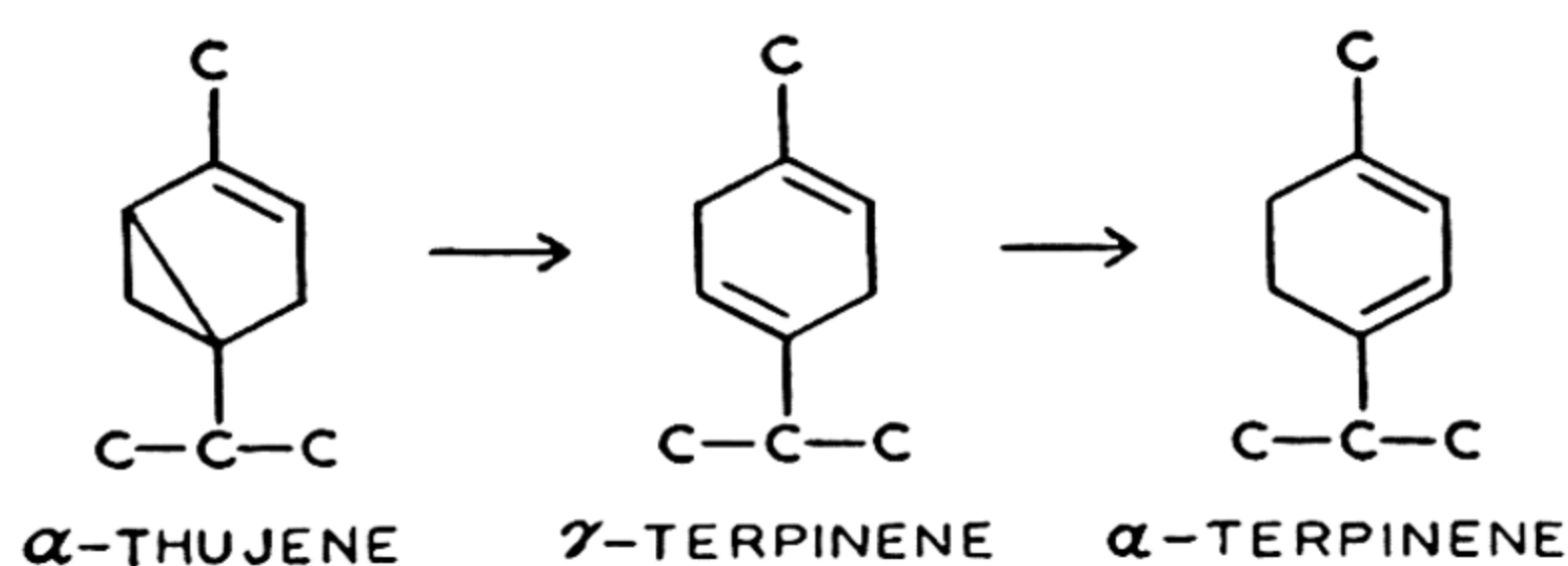
4. β -Curcumene isomerizes by cyclization, which may be highly competitive with aromatization of its two components.

BICYCLENES AND BICYCLENES WITH SATURATED SIDE-CHAINS

Isomerizations

Several examples of isomerization are available in the group of bicyclenes (*i.e.*, bicycloölefins) with saturated side-chains or without side-chains. *d*-2-Methyl-5-isopropylbicyclo[3.1.0]hexene-2 (*i.e.*, *d*- α -thujene) racemizes very slowly on mere standing.⁵⁴⁶ Formation of the *levo* modification is apparently the basis of this "inversion," but a decyclization-isomerization is another possibility.

Decyclization of α -thujene at its weakest point, the incorporated cyclopropane ring, should yield both 1-methyl-4-isopropylcyclohexadiene-1,4 (*i.e.*, γ -terpinene) and 1-methyl-4-isopropylcyclohexadiene-1,5 (which is α -phellandrene) under mild reaction conditions. Partially racemized *d*- α -thujene, when subjected to the rather severe action of alcoholic hydrochloric acid under reflux for 15 minutes, followed by a special treatment of the recovered hydrocarbons (containing also α -terpinene mono- and dihydrochlorides) with maleic anhydride in acetone, yielded 45 per cent of free γ -terpinene and 20 per cent of α -terpinene-maleic anhydride adduct.^{206b} A stepwise transformation of α -thujene into γ -terpinene and α -terpinene was postulated:

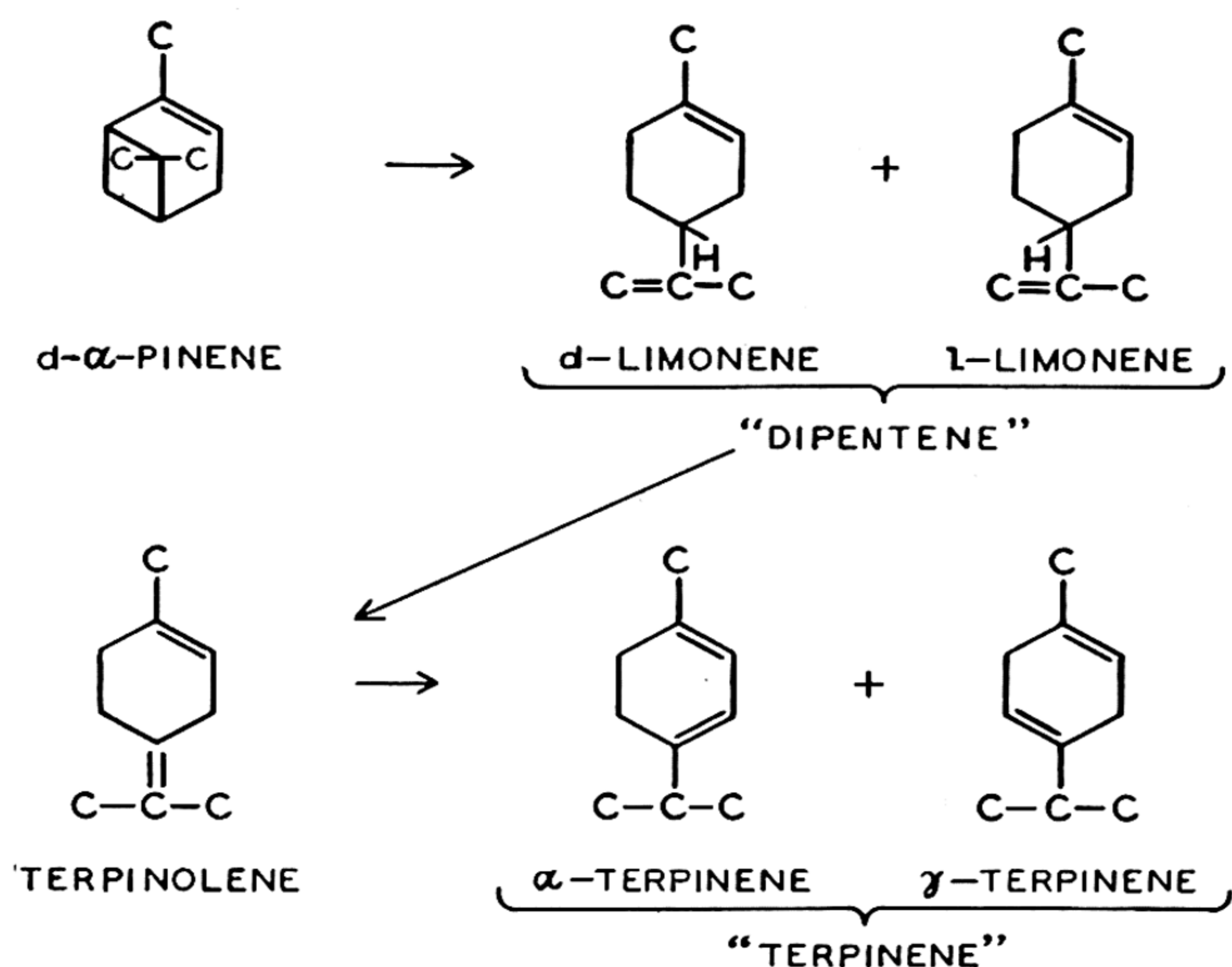


However, 3 per cent of *dl*- α -phellandrene-maleic anhydride adduct and 16 per cent of α -terpinene-maleic anhydride adduct were formed when α -thujene and maleic anhydride were heated together^{206b} in the customary manner.^{206a} A considerable amount of *p*-cymene was obtained as a by-product. α -Thujene yielded 7 per cent of α -terpinene-quinone

adduct, besides quinhydrone, when heated for 2 hours under reflux with quinone and alcoholic hydrochloric acid.^{206b}

2,6,6-Trimethylbicyclo[3.1.1]heptene-2 (*i.e.*, α -pinene) is a terpenic bicyclene that has been studied extensively. Its isomerization proceeds by a breaking and rearrangement of rings with the formation of open-chain, monocyclic, and bicyclic hydrocarbons. An isomerization of α -pinene into β -pinene has not been observed to date,^{466, 663} although an analogous shift of the double bond occurs in the formation of camphene.

The isomerization by scission of *one* ring occurs at moderate temperatures. Heating of α -pinene (American turpentine oil) for one hour at 250-270°⁶¹⁵ or for 2 hours at 300°^{60, 462} caused isomerization into dipentene and a partial polymerization. This "inversion" of optically active α -pinene by heat "without catalysts" leads always to dipentene¹¹² and not to *dl*- α -pinene, as has been reported erroneously.⁵⁵⁷ Catalysts lower the reaction temperature: active carbon,³⁷⁷ alumina,³⁹¹ thoria,¹⁰⁵ fuller's earth,⁶¹⁰ phosphoric acid,^{103, 255, 502} sulfuric acid,^{105, 149, 254, 615, 616, 617} and chloroacetic acid^{133a} have converted α -pinene into dipentene, terpinene, and terpinolene. Even treatment of *d*- α -pinene (French turpentine oil) with hydrogen (110-120 atm.) in the presence of copper oxide at 240°, or of iron, gives dipentene, rather than hydrogenated products.²⁷² Arsenic acid is a good catalyst for the formation of "terpinene," since it reacts readily with limonene.^{208, 209} The foregoing isomerizations of *d*- α -pinene can be summarized by the following reactions:

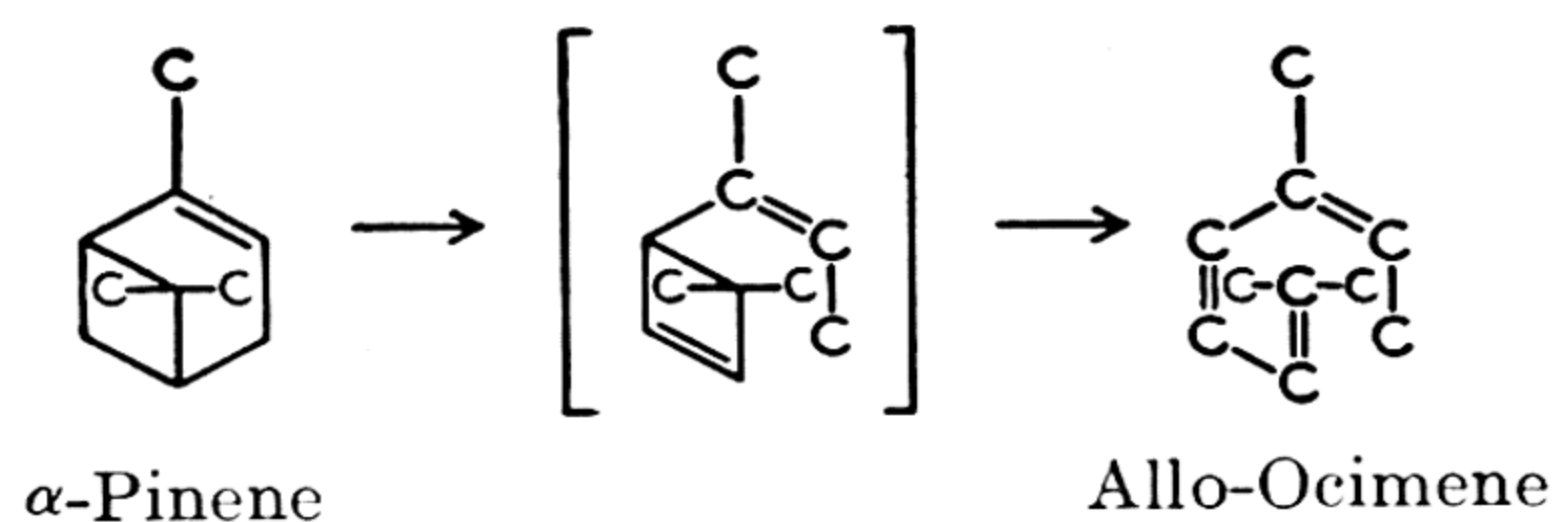


American turpentine oil (essentially α -pinene), heated at 100° for several hours with 25-per cent hydrochloric acid and alcohol, formed a little dipentene, together with a large amount of chlorinated products.⁶¹⁵ A mixture of American turpentine oil, alcohol, and nitric acid (sp. gr. 1.255), when heated slightly, also gave dipentene.⁶¹⁵

α -Pinene did not isomerize in the presence of 1.0*N* phosphoric acid. A treatment with 3.5*N* acid for 5 hours, however, gave camphene and dipentene, besides ethyl terpinyl ether, terpineol, and $C_{10}H_{16} \cdot H_3PO_4$.²⁵⁵ The use of 10*N* phosphoric acid resulted in the formation of terpinolene, *p*-cymene, and cineol.²⁵⁵ The production of dipentene and terpinolene, by heating α -pinene with phosphoric acid at 70-100°, is the subject of recent patents.^{541, 542} It has been stated that *l*- α -pinene, heated with acetic acid containing phosphoric acid, gives a considerable amount of *l*-limonene.⁴⁴⁸

The "inversion" of α -pinene by sulfuric acid gives terpinolene (b.p. 185-190°).^{616, 617} The heating of American turpentine oil, with sulfuric acid (sp. gr. 1.64) plus alcohol for one day at 100°, gave cymene and a fraction (b.p. 180-190°) containing "terpinene."^{615, 616} Dipentene may be also a product of this reaction.¹⁹¹ Turpentine oil (α -pinene), when treated carefully for 2-3 days with concentrated sulfuric acid, and thereafter steam-distilled, gave a main fraction (b.p. 170-190°) containing "terpinene."⁶¹⁷ As an example of the complexity of the isomerization of turpentine oil (essentially α -pinene), by strong acid, there can be cited the case of the formation of complex mixtures^{13, 14, 138, 461, 462, 463, 464, 617} designated at times as "terebene" and as "terpilene." These mixtures have been prepared, for example, by agitating a large volume of rectified turpentine oil (12 liters) with 50-per cent sulfuric acid (800 g.) for one day.¹⁴⁹ The product was found to contain camphene, limonene, dipentene, α -terpinene, γ -terpinene, terpinolene, besides cymene, cineol (2 per cent), and 4 new substances.¹⁴⁹ The yield is only 33 per cent, the remainder is polymers.¹⁴⁹ Russian turpentine oil (a mixture of α - and β -pinenes) has been treated for several days with sulfuric acid (sp. gr. 1.64) and alcohol at 100° in order to prepare γ -terpinene and terpinolene.^{669a} The β -pinene component probably is transitionally isomerized to α -pinene, since acids are known to convert β -pinene into α -pinene.

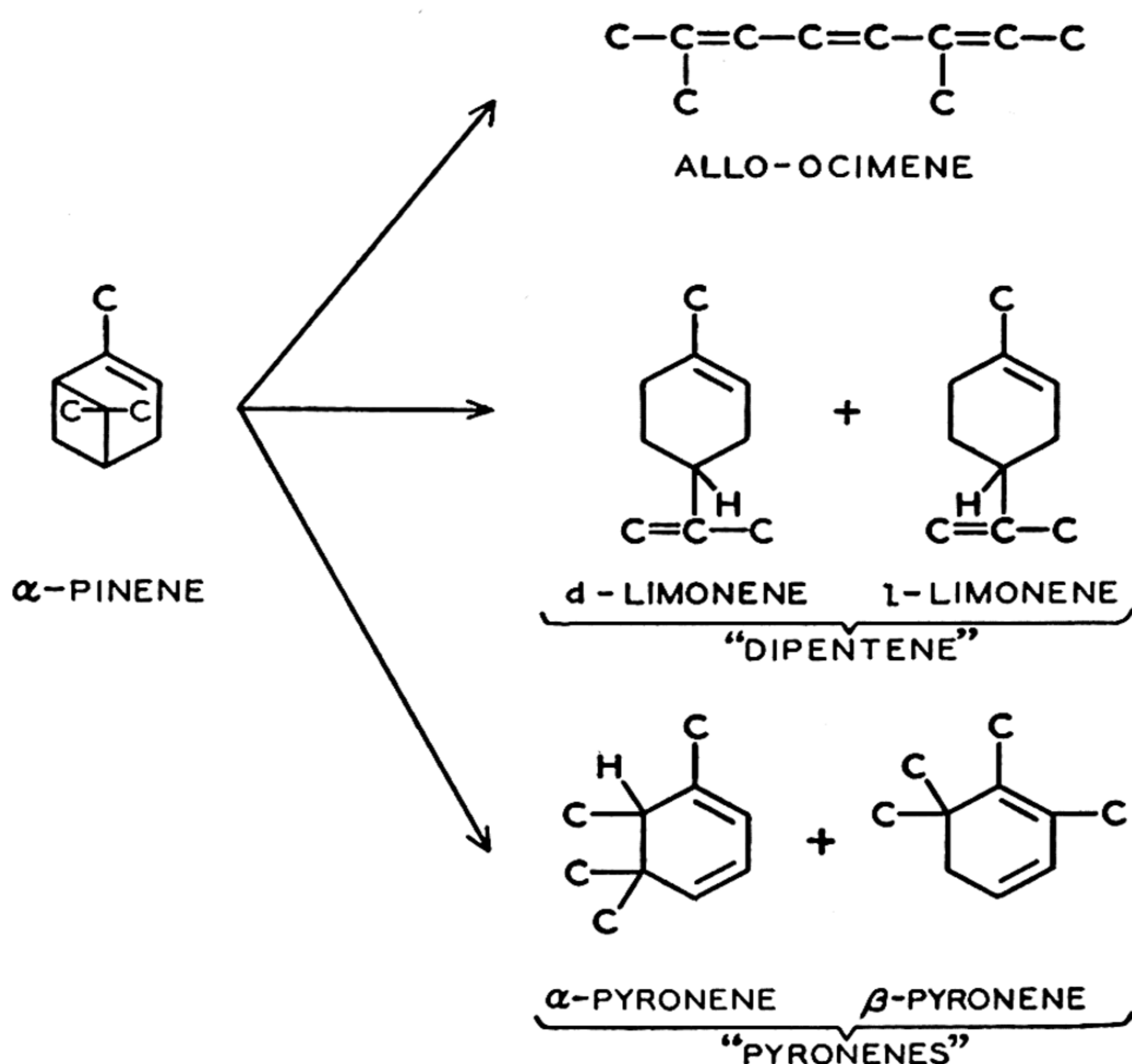
A severe isomerization of α -pinene, with rupture of *both* rings, results in the formation of allo-ocimene, which is an aliphatic isomer. The probable course of this reaction may be the intermediary formation of an unstable cyclobutene: ⁹



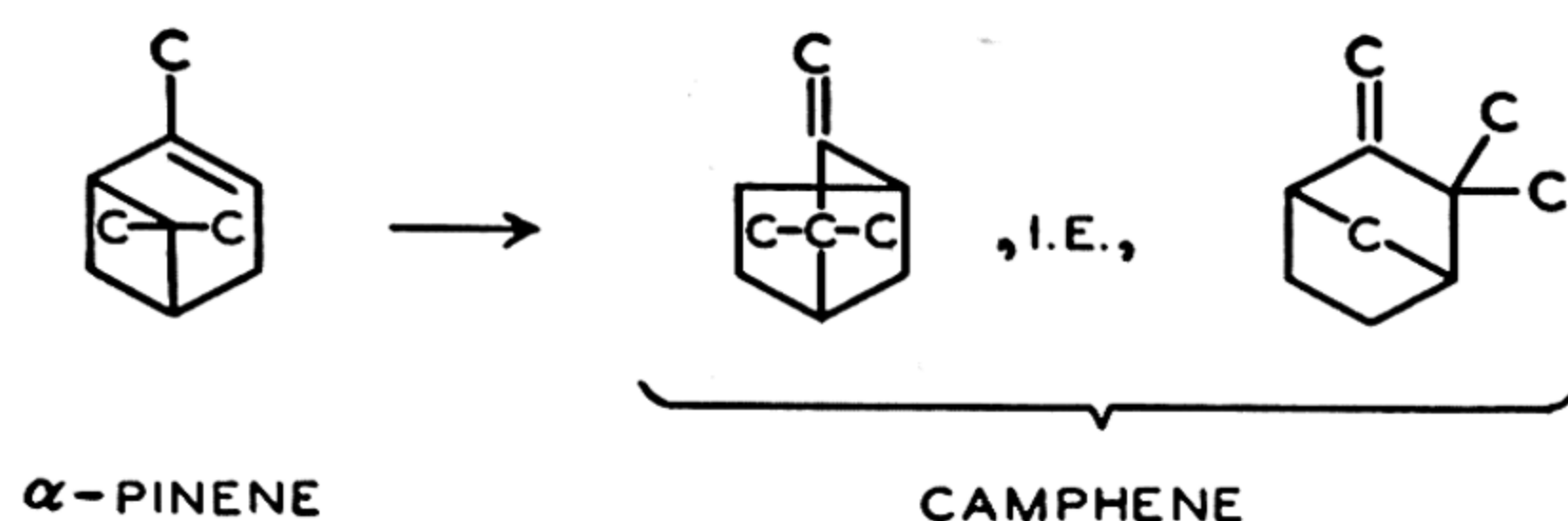
α -Pinene vapors, when passed over a copper chromite catalyst (Adkins') at 375°, or over a cobalt-thorium catalyst (Fischer and Koch's) at 340-400°, gave dipentene and allo-ocimene.¹⁰ Similarly, the passage

of α -pinene vapors over reduced copper at 340-350°, or through a tube filled with chips of "Suprax" glass at approximately 350°, resulted respectively in 26.5 and 24.6 per cent of allo-ocimene.^{8, 11} Even ordinary soft glass is effective, yielding 26 per cent of allo-ocimene.⁸ These yields were reduced to 17 per cent at 380-390°.⁸ This seems to indicate that temperature, time of contact, and heat-transfer coefficients are important factors in this isomerization, rather than the catalyst type. The conduction of *d*- α -pinene, as vapor in nitrogen through a "Pyrex" glass tube heated at 370-375° gave a product containing 6, 6, 40, and 42 per cent of α -pyronene, β -pyronene, allo-ocimene, and dipentene, respectively.^{217a} The idea has been advanced⁸ that allo-ocimene is a very common product in the isomerization of α -pinene. However, it has probably been missed by previous investigators because of the application of too high temperatures (600-700°),⁴⁹⁶ or by mistaking allo-ocimene for a polymerization product.³⁹⁰

Passage of α -pinene over copper gauze at 300-350° yielded allo-ocimene, dipentene, and about 50 per cent of α - and β -pyronenes.¹⁴⁴ The yield of allo-ocimene is 30 per cent at 340°.¹⁴⁸ *dl*- α -Pinene, when treated similarly at 350°, gave *dl*- α - and β -pyronenes.¹⁴⁵ Recent work¹⁴⁶ indicates that β -pyronene possesses the structure of 1,2,6,6-tetramethylcyclohexadiene-1,3, possibly because of a shifting of both double bonds in α -pyronene. The earlier assignment¹⁴⁴ of 1,5,5-trimethyl-6-methylene-cyclohexene-1 to β -pyronene is now reserved for cyclomyrcene. The formation of dipentene and α -pyronene involves ring scission and the migration of hydrogen (from one of 3 carbon atoms, thereby forming a double bond):



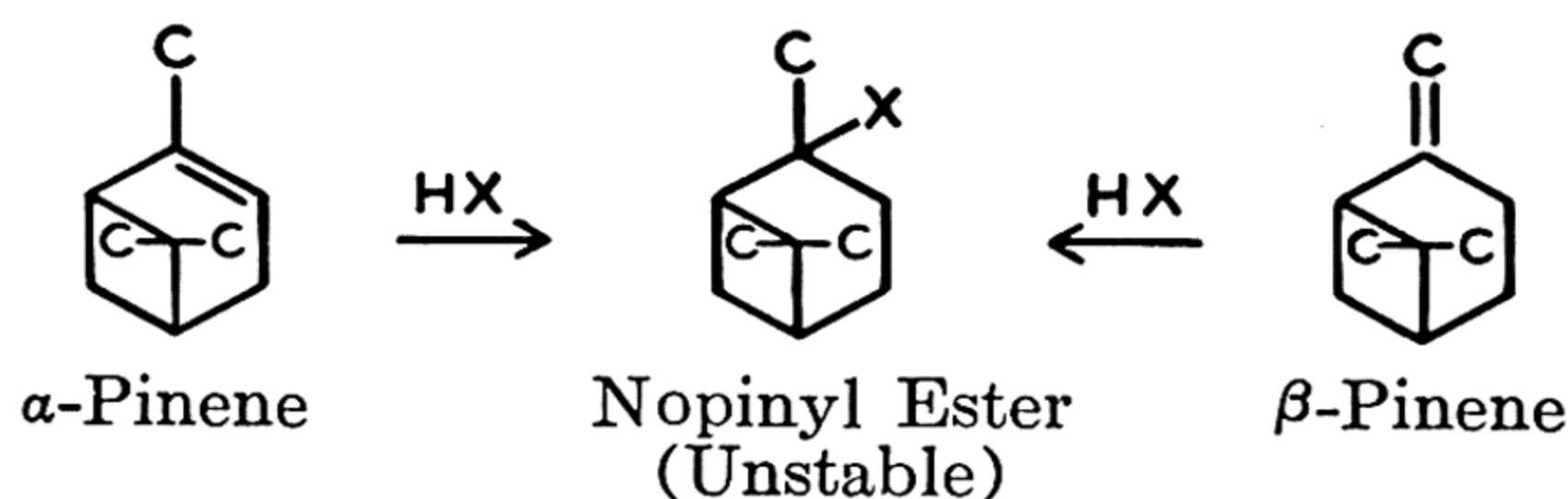
Isomerization of α -pinene by a decyclization occurring at other places in the molecule has been reported. The possibility of such a change is indicated by the conversion of α -pinene into camphene via acids or acidic catalysts:



The isomerization of α -pinene into camphene occurs in the presence of active carbon,^{202, 377} red phosphorus,^{91, 383} alumina,^{91, 383} bauxite,⁵⁸⁶ silica,^{91, 383, 505} kieselguhr,^{91, 383} thoria,¹⁰⁵ aluminum phosphate,^{91, 383} calcium phosphate,^{91, 383} kaolin,^{91, 383, 586} clays,^{91, 236, 327, 349a, 383, 586} fuller's earth,^{91, 235, 383} acid-treated permutite,⁵⁰⁵ various acid phosphates,^{508, 514, 601a} highly acidic molybdates, tungstates, or vanadates,^{504, 504a, 510} acid phosphotungstates,⁵¹⁴ $\text{CoSO}_4 \cdot \text{H}_2\text{O}$,^{503, 513} $\text{FeSO}_4 \cdot \text{H}_2\text{O}$,^{503, 513} $\text{MgSO}_4 \cdot \text{H}_2\text{O}$,^{459a, 503, 509, 513} NaHSO_4 ,⁵⁰⁸ $\text{NiSO}_4 \cdot \text{H}_2\text{O}$,^{503, 509, 513} $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$,^{503, 513} antimonie acid,^{502, 511a, 512, 514, 601a} meta-boric acid,^{502, 508} ortho-boric acid,⁵¹⁴ molybdic acid,^{502, 514} arsenomolybdic acid,⁵¹⁴ phosphomolybdic acid,^{502, 514, 601a} silicic acid,^{502, 508, 514} phosphostannic acid,^{511a, 514} titanie acid,^{502, 508, 514, 601a} tungstic acid,^{502, 514, 601a} borotungstic acids,⁵¹⁴ phosphotungstic acid,^{502, 514} silicotungstic acids,⁵¹⁴ vanadic acid,^{502, 508, 514, 601a} silicovanadic acid,⁵¹⁴ alcoholic hydrochloric acid,²⁵⁶ phosphoric acid,⁵⁰² alcoholic phosphoric acid,²⁵⁵ borophosphoric acid,^{511, 511a, 514} sulfuric acid,^{149, 462, 464} sulfonic acids,⁵⁰⁸ formic acid,⁴⁶⁰ acetic acid,^{35, 36, 75, 662} boracetic acid,⁵¹⁴ chloracetic acid,^{133a} oxalic acid,^{133a, 508} aluminooxalic acid,⁵¹⁴ chromooxalic acid,^{502, 514} benzoic acid,⁷⁶ salicylic acid,^{133a} o-benzoylbenzoic acid,^{133a} phthalic acid,⁵⁰⁸ acetic anhydride with boric anhydride,^{268, 269} acetic anhydride with ortho-boric acid,²⁶⁸ colophony,⁴³⁹ phenol,³²² picric acid,^{133, 322} and numerous substituted phenols.³²² These catalysts represent a *whole range of acidities* and yields of camphene up to 85 per cent! The suitability of fuller's earth in the formation of camphene from α -pinene has been questioned.⁶¹⁰

The formation of camphene from α -pinene and acids is considered to be an example of the "delayed isomerization" and "right-shift" proposed for conversions of β -pinene into camphene. It involves a double Wagner-rearrangement: that of α -pinene into bornyl esters^{534, 614} and that of isobornyl esters into isocamphanyl esters.^{369, 370} With hydrogen chloride, the logical first step is formation at -60° ³⁷⁰ of the exceedingly unstable true pinene-hydrochloride.¹⁷ The transformation of α -pinene into camphene via acids and acidic catalysts appears to proceed in the

same 5 steps as proposed for the conversion of β -pinene into camphene, since the initial steps give identical nopinyl esters:



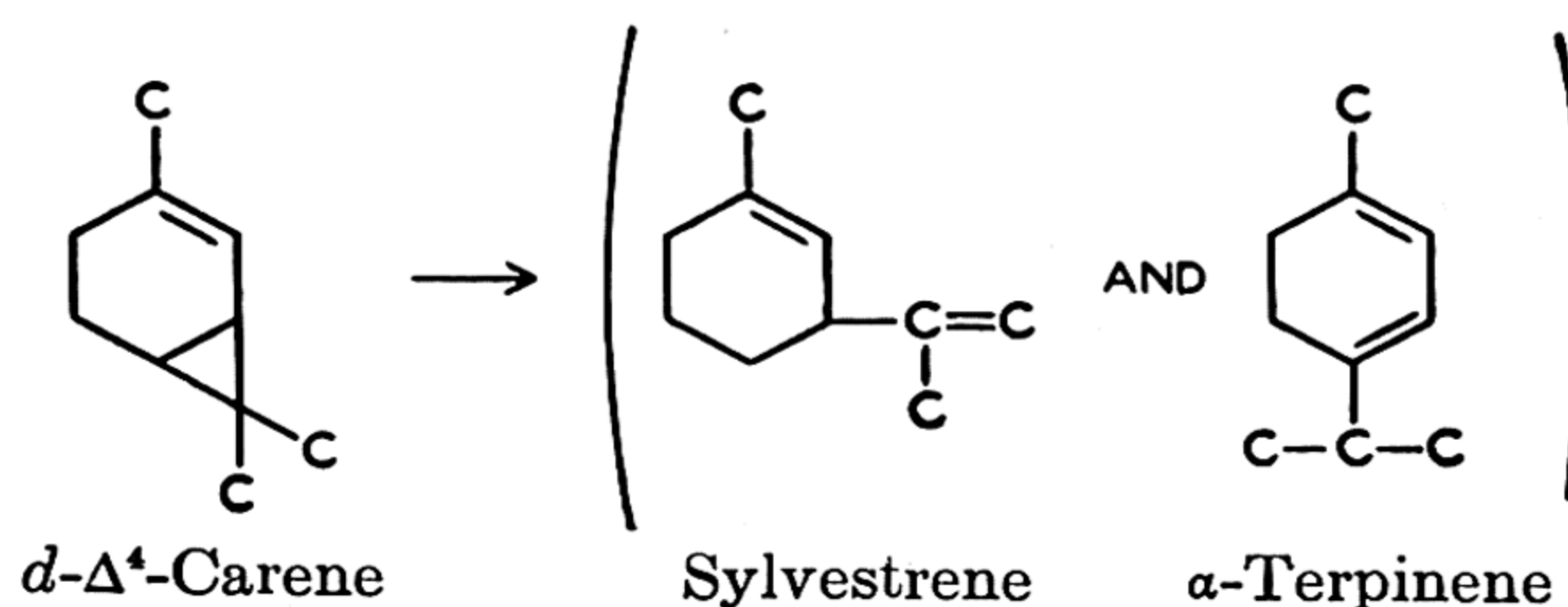
A considerable amount of work has been carried out on the action of *organic* acids on α -pinene. Unfortunately, considerable confusion exists in the literature as to the structures of the usual "hydration" products⁷⁷ and the modes of their formation.^{36, 322} *d*- α -Pinene, when treated for over two months with formic acid, gave *d*-camphene, *d*-limonene, dipentene, α -terpinene and terpinolene, as isomers, along with recovered *d*- α -pinene, formic acid, *d*-diterpilene, bornyl formate, *d*-4-terpinenyl formate, and *d*- α -terpinyl formate.⁴⁶⁰ The treatment of *l*- α -pinene with formic acid gives *l*-limonene.^{78, 328} *d*- α -Pinene, when heated at 100° with acetic acid, formed *d*-limonene, *d*-bornyl acetate, *l*-bornyl acetate, and *d*- α -terpinyl acetate.³²⁸ *l*- α -Pinene, treated with acetic acid, gave various proportions of *l*-limonene and *l*-camphene, depending probably on whether the acid used was or was not heated and anhydrous.^{35, 36, 75, 662} Other products formed at the same time are *l*- α -terpinyl acetate,^{35, 36, 74, 75, 78, 171} (*Ld*)-fenchyl* acetate,^{35, 36, 74, 75} *l*-bornyl acetate,^{35, 36, 74, 75, 662} isobornyl acetate,^{35, 36} and terpin hydrate.⁷⁸ *d*-Limonene was found in a free state among the products of esterification of *d*- α -pinene by means of acetic acid containing acetic anhydride and Japanese acid clay.^{327a} *l*- α -Pinene, when heated with benzoic acid, formed *l*-camphene, *l*-limonene, *l*-bornyl benzoate, (*Ld*)-fenchyl benzoate, and colophony.⁷⁶ The action of phenol and its various substitution products (*o*-cresol, resorcinol, methyl salicylate, *p*-nitrophenol, *p*-nitro-*m*-cresol, *m*-dinitrophenol, dinitro-*o*-cresol, 2,6-dinitro-*p*-cresol, picric acid, 2,4,5-trinitro-*m*-cresol, trinitrothymol, tribromophenol, and trichlorophenol) upon heated *l*- α -pinene gives *l*-camphene and, in some cases, also dipentene, diterpene, a bornyl phenolate, and a trace of water.³²²

l- α -Pinene, when treated with acetic and boric anhydrides at 90-95°, formed *l*-camphene and dipentene, together with bornyl, isobornyl and fenchyl acetates.²⁶⁸ α -Pinene, heated at 110-120° for 15-18 hours with acetic acid, acetic anhydride, plus boric anhydride, yielded camphene, dipentene, α -terpinene, terpinolene, along with *p*-cymene, bornyl acetate, isobornyl acetate, and possibly also α - and β -fenchyl acetates.²⁶⁹ *l*- α -Pinene, when heated with acetic anhydride containing ortho-boric

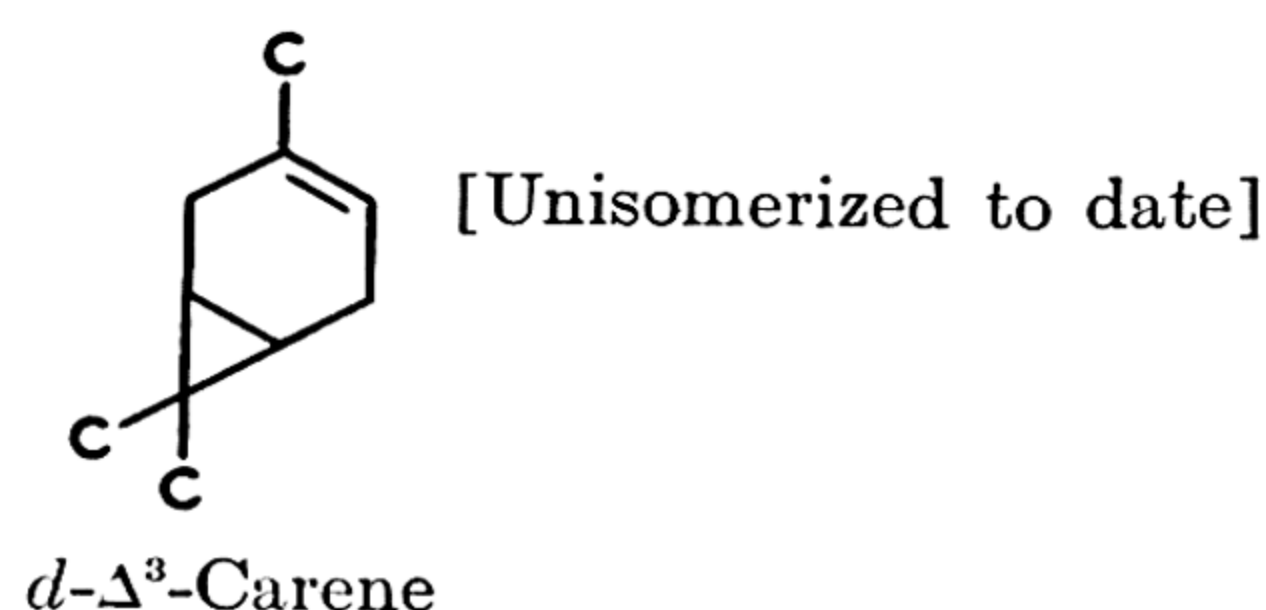
* The symbol *Ld* describes both the actual optical rotation (*d*) and the starting point for a synthesis from fenchone (*l*-form), according to Wallach.^{620a}

acid gave *l*-camphene, dipentene, cymene, α -fenchyl acetate, β -fenchyl acetate, bornyl acetate, isobornyl acetate, and possibly α -terpinyl acetate and the acetate of some diterpene.²⁶⁸

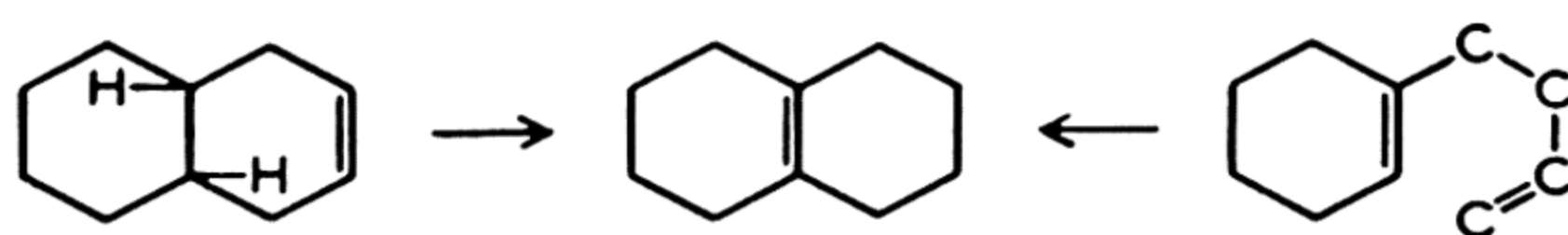
d-3,7,7-Trimethylbicyclo[4.1.0]heptene-2 (*i.e.*, *d*- Δ^4 -carene), heated at 280° for 4 hours, gave sylvestrene and α -terpinene.⁵³⁸ Treated with boiling acetic acid, it formed α -terpinene: ⁵³⁸



d-3,7,7-Trimethylbicyclo[4.1.0]heptene-3 (*i.e.*, *d*- Δ^3 -carene) "passed unchanged" through a "Suprax" glass tube at 400°.¹²



The isomerization of 1,6-*trans*-bicyclo[4.4.0]decene-3 (*i.e.*, *trans*-1,2,3,4,4a,5,8,8a-octahydronaphthalene or *trans*- Δ^2 -octalin) into bicyclo[4.4.0]decene-1[6] (*i.e.*, 1,2,3,4,5,6,7,8-octahydronaphthalene or $\Delta^{9,10}$ -octalin), which occurs upon heating under reflux with phosphorus pentoxide for 3 hours at 140°, ³⁵³ is of interest in connection with the cyclization of 1-(3-butenyl)cyclohexene-1. This cyclization involves either the intermediary formation of 1,2,3,4,4a,5,6,8a-octahydronaphthalene or the direct formation of 1,2,3,4,5,6,7,8-octahydronaphthalene. The isomerization of *trans*-1,2,3,4,4a,5,8,8a-octahydronaphthalene into 1,2,3,4,5,6,7,8-octahydronaphthalene probably involves the intermediary formations of 1,2,3,4,4a,5,6,8a-octahydronaphthalene and 1-(3-butenyl)cyclohexene-1, rather than that of 1,2,3,4,4a,5,6,7-octahydronaphthalene. The last hydrocarbon is a strained form, according to Bredt's rule,⁸⁹ since it has a double bond adjacent to the juncture of 2 fused rings. Under Anthracenes (*supra*), it will be seen that the 3-butenyl group probably enters readily into "alkylation-dealkylation" isomerizations:



The isomerizations of bicyclenes and bicyclenes with saturated side-chains are listed in Table 27, page 330.

Conclusions

The complicated isomerizations of the bicyclenes can be summarized only for the few members investigated to date. Even so, several theoretical possibilities remain to be investigated in the observed examples, such as the relative stability of various atomic and valence bridges.

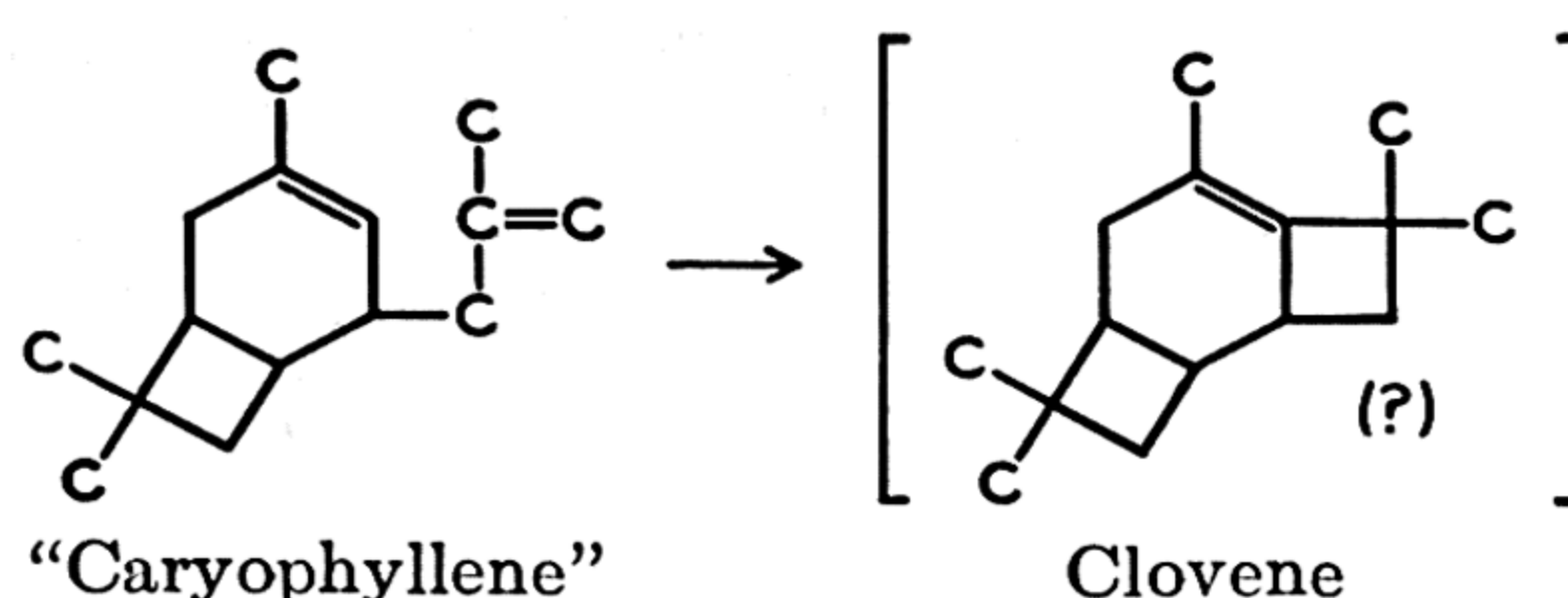
1. The shift of the double bond observed in the case of *trans*-1,2,3,4,4a,5,8,8a-octahydronaphthalene does not have a counterpart in the numerous isomerizations shown by α -pinene. The double bond of α -pinene apparently stays intact in all paths except that leading to camphene!

2. The complexity of the transformation of α -pinene into camphene is shown by its numerous steps in the presence of acidic catalysts. In such cases where the intermediary salts cannot form (as with heat or certain catalysts), it is suggested that similar steps are operative. Analogous active forms of the molecule (bicyclo-diyls without a negative ion) are suggested as being responsible for the isomerization.

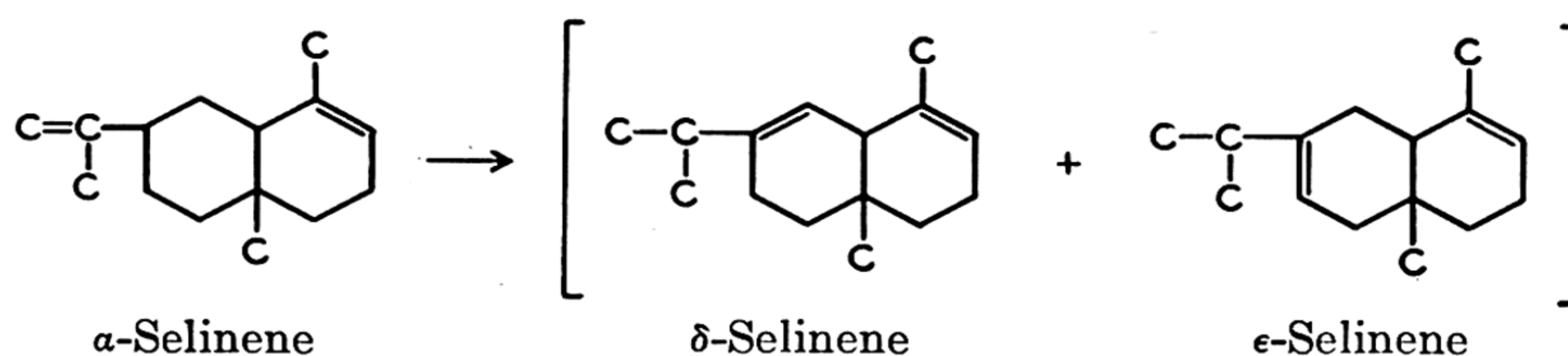
BICYCLENES WITH UNSATURATED SIDE-CHAINS

Isomerizations

Ordinary "caryophyllene," which is a mixture of two bicyclic sesquiterpenes from clove oil, is isomerized by treatment with mixed acetic and sulfuric acids, according to the Wallach-Walker⁶³³ and Bertram-Walbaum⁶⁵ method of esterification. An early observation⁶³³ states that ordinary "caryophyllene," when heated for 12 hours with acetic acid plus dilute sulfuric acid, gives caryophyllene hydrate ($C_{15}H_{25}OH$, m.p. 96° , hence β -iso-caryophyllene alcohol⁴⁸⁸), which can be dehydrated by phosphorus pentoxide to "clovene" (b.p. $261-263^\circ$). The latter should be taken as the higher-boiling component of 2 tricyclic caryophyllenes, which comprise the usual product.^{137, 488} Other observations^{136, 137} indicate that the treatment with mixed acetic and sulfuric acids gives simultaneously "isocaryophyllene alcohol" (caryophyllene hydrate), clovene (b.p. $261-263^\circ$), and the lower-boiling component of the tricyclic sesquiterpene.¹³⁶ β -Caryophyllene (bicyclic), when heated under reflux with formic acid for several days, gave "clovene," the formate of a tricyclic alcohol (probably β -iso-caryophyllene formate), and unchanged caryophyllene.⁴⁶⁹ Treatment of "caryophyllene" (b.p. $123-124^\circ$ at 16 mm. Hg) alternately with ethereal sulfuric acid and sodium hydroxide solution formed clovene, α -iso-caryophyllene alcohol (m.p. 116°), and β -iso-caryophyllene alcohol.⁴⁸⁸ The cyclization of caryophyllene into clovene can be formulated tentatively, on the basis of a structure⁴⁸³ proposed for "caryophyllene," as follows:



d- α -Selinene was converted readily by alcoholic sulfuric acid into a dextrorotatory product, probably δ - and ϵ -selinenes:⁴⁹²



l-Sclarene, a bicyclic diterpene obtainable by dehydration of the naturally occurring sclareol, isomerized incompletely to a tricyclic, via cyclization, when heated at 120° for 4 hours with formic acid.⁴⁸⁹ Sclarene is considered to be a bicycene at this point for the purpose of classification, since its structure is unknown.⁴⁸⁷

The experimental data on isomerizations of the bicyclenes with unsaturated side-chains are given in Table 28, p. 352.

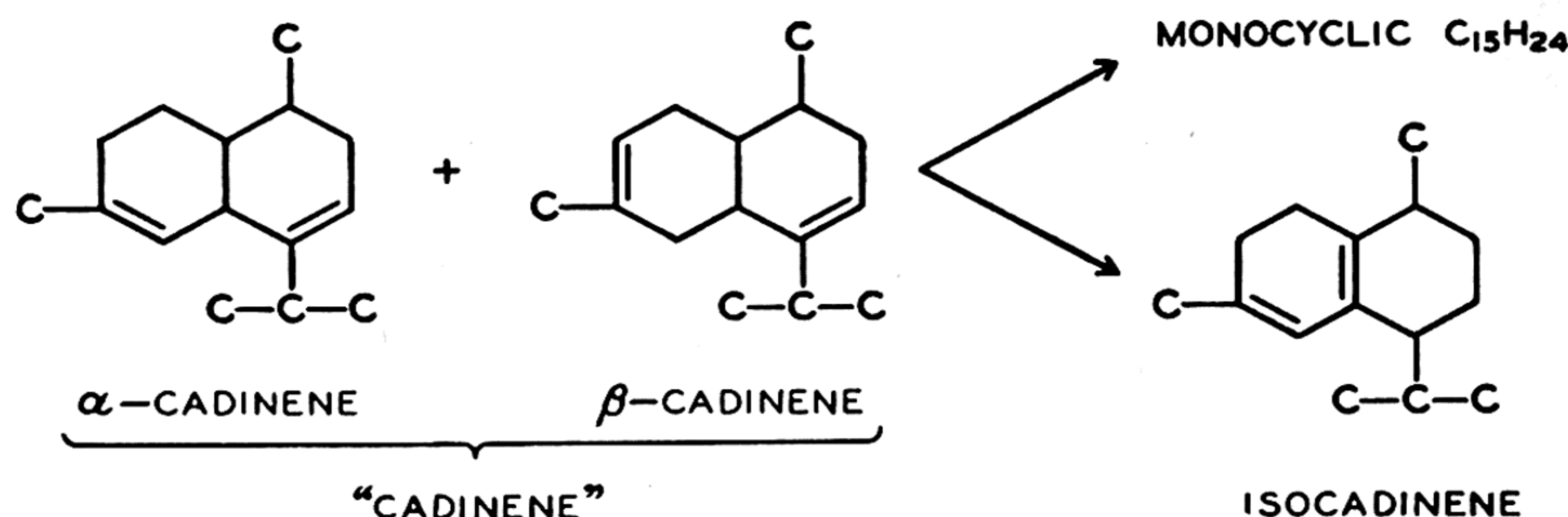
Conclusions

1. The bicyclenes with unsaturated side-chains undergo an isomerization into bicyclodienes or tricyclenes.
2. These products are those expected on the basis of isomerization with acidic catalysts, namely, isomers formed by the shift of double bonds into rings, and/or by cyclization.

BICYCLODIENES WITH SATURATED SIDE-CHAINS

Isomerizations

The group of bicyclodienes (bicyclodiolefin) has not been studied extensively. *l*-Cadinene (regenerated) changed partly into a levorotatory monocyclic sesquiterpene when heated at 330° in a bomb tube.⁵³⁶ Cadinene, heated under reflux for 36 hours with 57-per cent sulfuric acid, gave an isomer of increased boiling point and greater density,⁴⁹³ thereby confirming an earlier observation that *l*-cadinene is isomerized when heated for a long time with dilute sulfuric acid.⁶³³ *l*-Cadinene (regenerated) gave isocadinene when heated at 100° for 8 hours with acetic acid plus sulfuric acid (Bertram-Walbaum method) or heated at 230-235° for 24 hours with acetic acid in a bomb tube.²⁴⁶

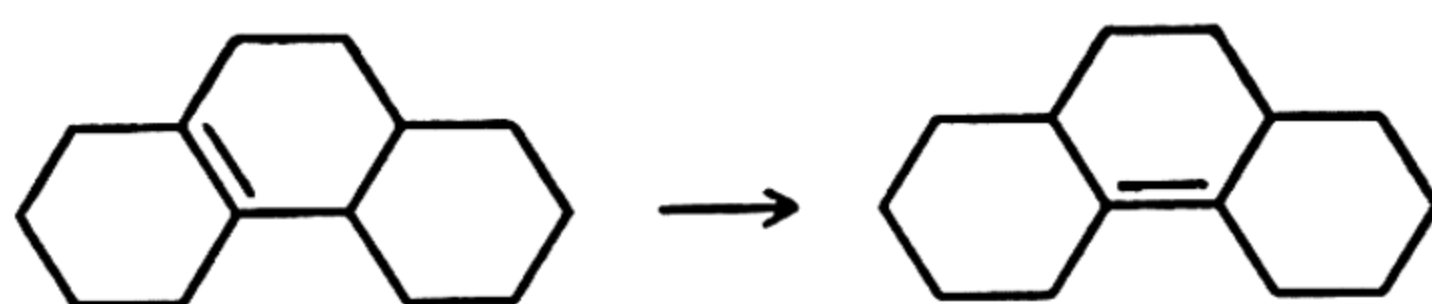


The experimental data are given in Table 29, p. 352.

TRICYCLENES AND TRICYCLENES WITH SATURATED SIDE-CHAINS

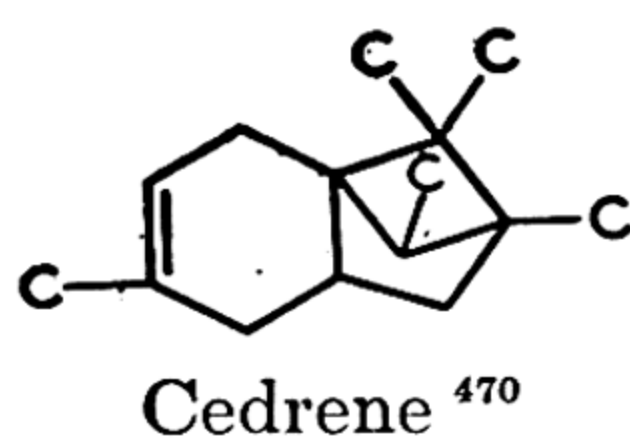
Isomerizations

Mere distillation (10-26 mm. Hg) of $\Delta^{11,12}$ -dodecahydrophenanthrene gave the more symmetrical $\Delta^{12,13}$ -dodecahydrophenanthrene:¹⁵⁰

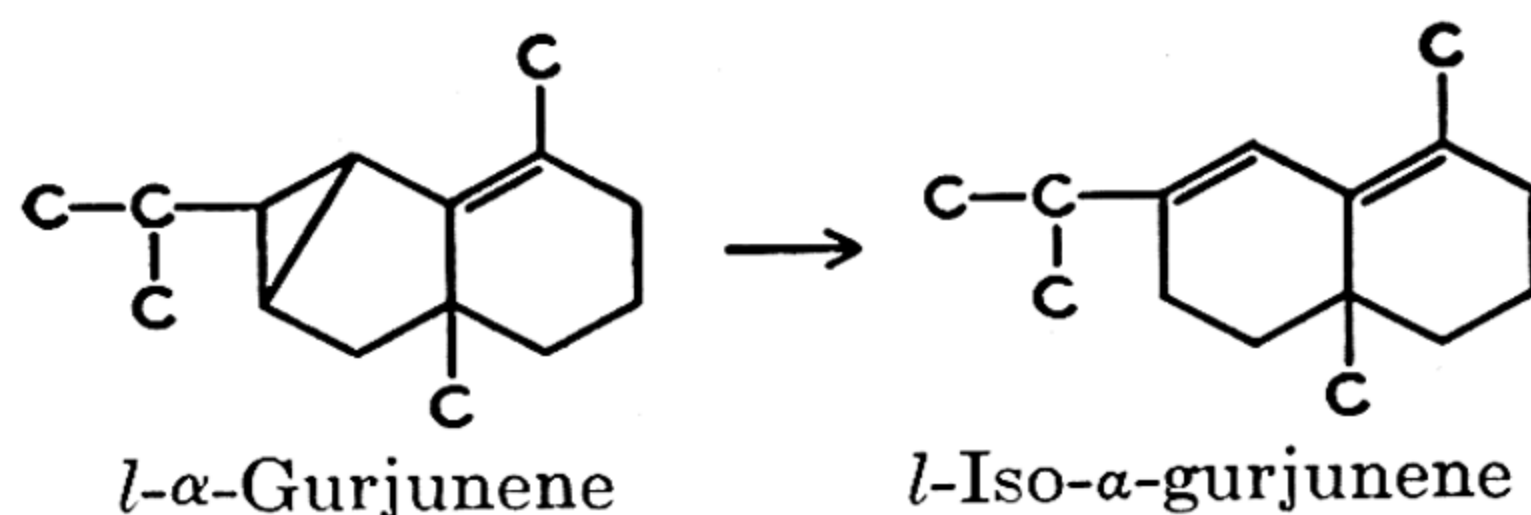


This reaction is accompanied by a slow dismutation into octahydro and tetradecahydro phenanthrenes.

Cedrene, heated under reflux with formic acid for several days, gave about 50 per cent of a lower-boiling tricyclic isomer.⁴⁶⁹ Cedrene is definitely a tricyclene;³⁶³ its structure is stated to be probably:



l- α -Gurjunene (*i.e.*, *l*-tricyclene-gurjunene) when heated at 330° for 12 hours in a bomb tube formed *dl*- α -gurjunene and underwent a disproportionation into a monoterpene and diterpene.⁵³⁶ *l*- α -Gurjunene, heated at 100° for 2 hours with acetic acid plus sulfuric acid, was decyclized to a bicyclic isomer, *l*-iso- α -gurjunene:⁵⁹¹



d- β -Gurjunene (*i.e.*, *d*-tricyclo-gurjunene), treated with hydrogen chloride plus acetic acid, gave similarly the bicyclic, *l*-iso- β -gurjunene.⁵⁹¹ The structures of these two isomers are unknown.

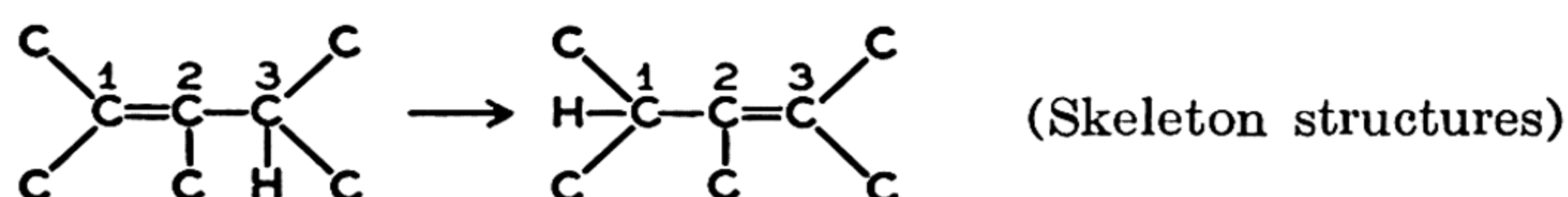
l-Sesquichamene is a tricyclic sesquiterpene of undetermined structure but known to be a tricyclene related to *d*-cedrene and *d*- β -gurjunene.^{294, 363, 364} *l*-Sesquichamene, when treated for 1.5 hours with alcoholic sulfuric acid at 40-50°, gives *l*-isosesquichamene, which is a bicyclic isomer according to molecular-refraction measurement.²⁹⁴

Isomerizations of tricyclenes and tricyclenes with saturated side-chains are listed in Table 30, p. 352.

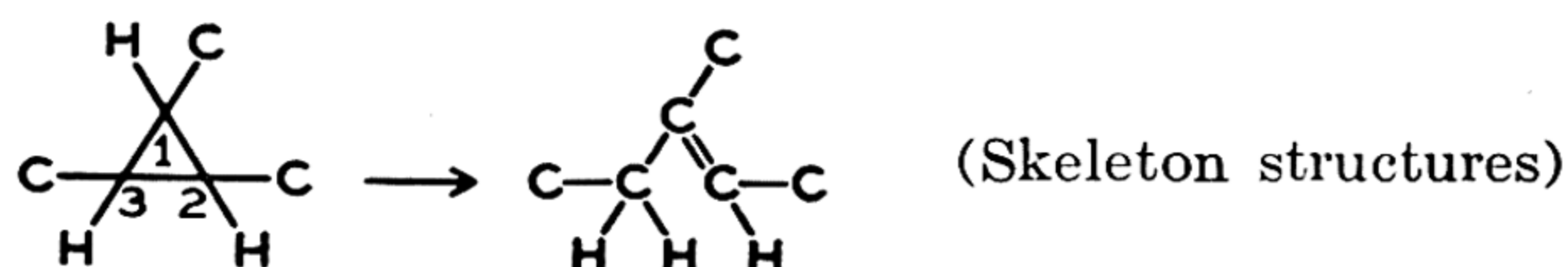
Conclusions

1. Isomerization of tricyclenes in two cases (with and without saturated side-chains) was accompanied by disproportionation, which is reflective of labile hydrogen behavior. Moreover, the isomerizations in these instances are also the result of hydrogen transfer.

2. $\Delta^{11,12}$ -Dodecahydrophenanthrene exhibits isomerization by 1:3 hydrogen shift in the following manner:



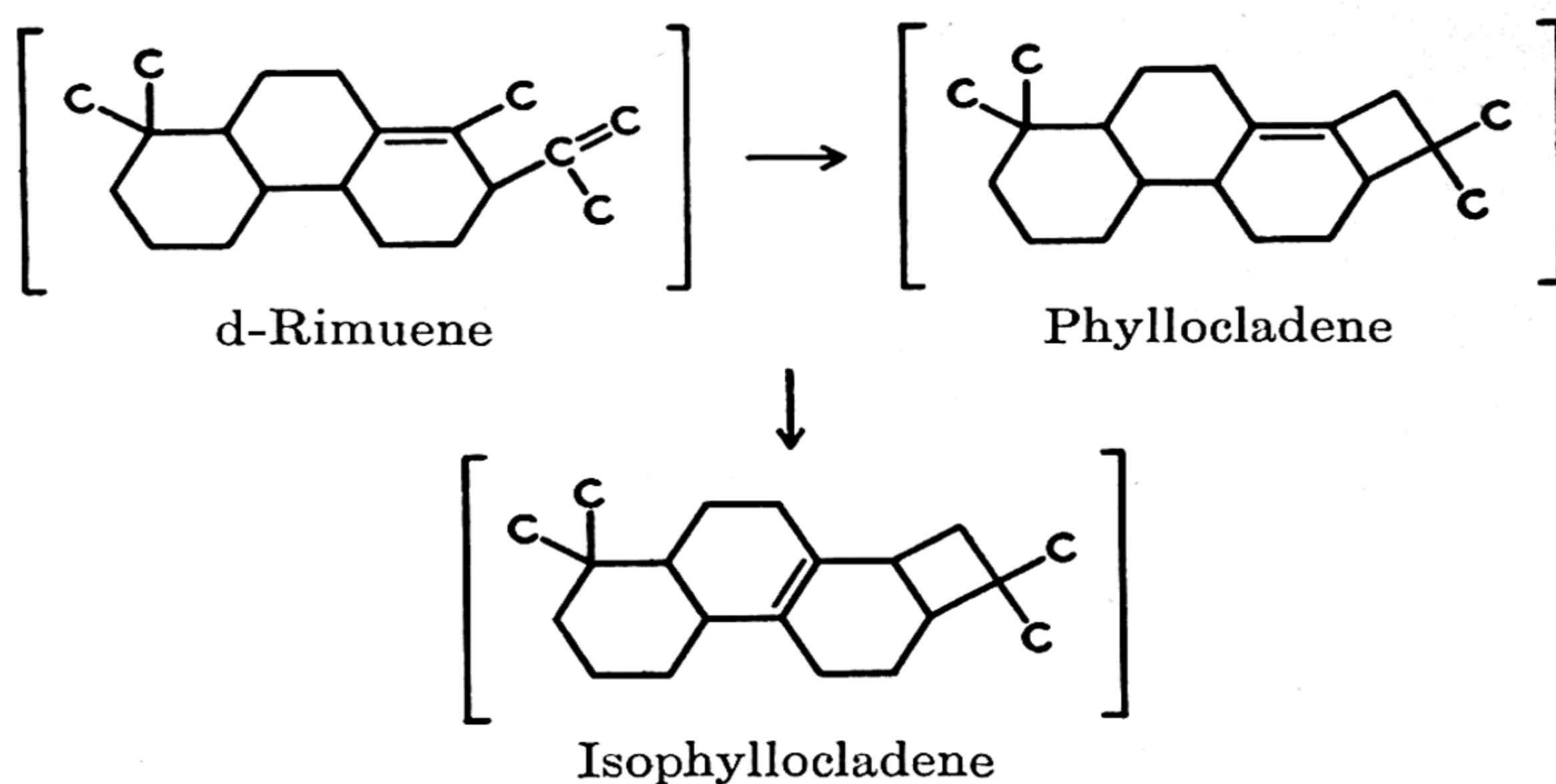
3. Analysis of the isomerization of *l*- α -gurjunene indicates the same type of 1:3 hydrogen transfer in the decyclization of incorporated cyclopropane rings:



TRICYCLENES WITH UNSATURATED SIDE-CHAINS

Isomerizations

d-Rimuene, a diterpene or tricyclene with an unsaturated side-chain,^{40, 87, 100} probably gives phyllocladene when heated alone to the boiling point,³⁶⁷ and isophyllocladene when heated under reflux with formic acid for 48 hours.⁴⁰ The first step in the last isomerization is probably the formation of phyllocladene by cyclization.⁸⁷ It may be remarked that the formulas, proposed by various investigators, for rimuene,^{40, 87} phyllocladene^{90, 606} and isophyllocladene⁶⁰⁶ are inconsistent, and introduce serious discrepancies in structures. The present authors suggest, for classification purposes, the following structures for rimuene, phyllocladene, and isophyllocladene, which are based upon related formulas for caryophyllene and clovene:

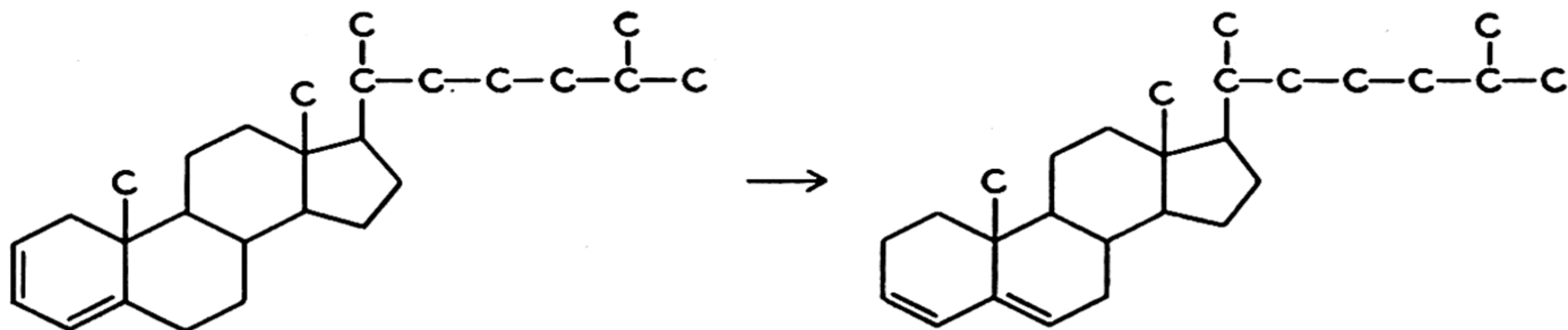


These formulas, however, have the disadvantage of a deviation (isomerization) from the usual rule of 4 isoprene residues for diterpene structures. The experimental data are included as Table 31, p. 354.

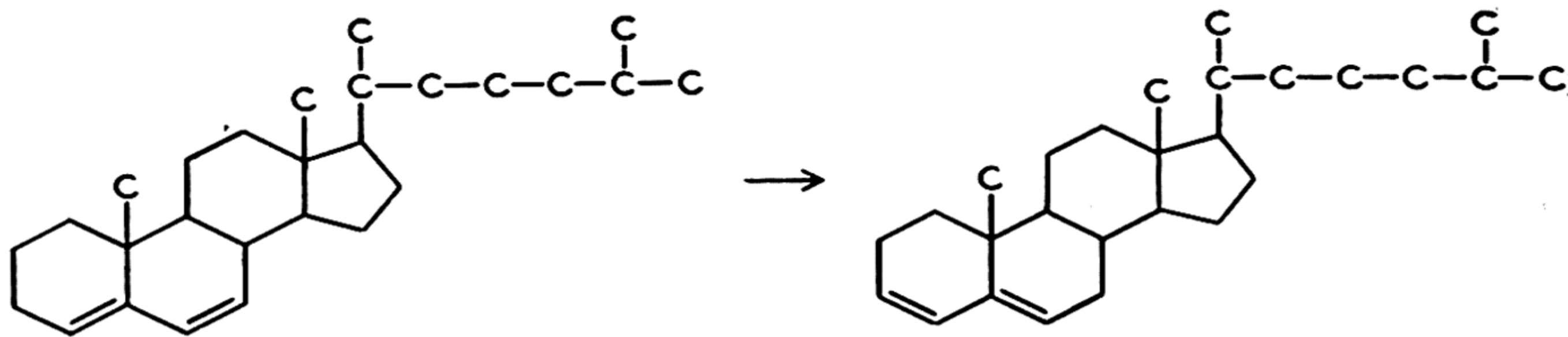
Isomerizations

TETRACYCLENES

d-2,4-Cholestadiene is isomerized to *l*-3,5-cholestadiene (cholesterylilene) by a treatment with alcoholic hydrochloric acid for 6-26 hours:⁵⁶⁵

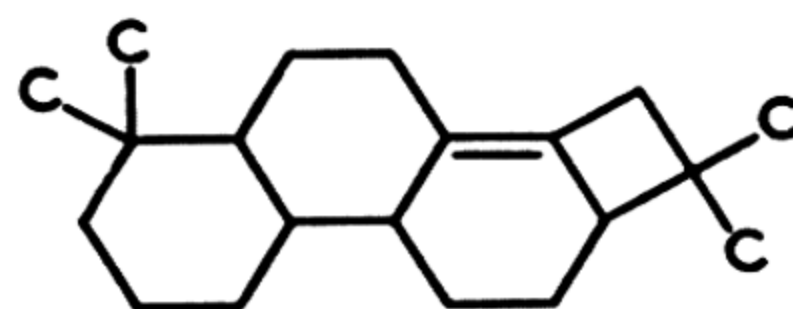


d-4,6-Cholestadiene gives *l*-3,5-cholestadiene when its solution in chloroform is subjected to hydrogen chloride gas for 3 hours:^{150a}



The isomerization of *d*-phyllocladene (also known as dacrene or sciadopitene) into *d*-isophyllocladene (*i.e.*, isodacrene or isosciadopitene) takes place on heating at 100° with alcoholic sulfuric acid for a few minutes⁹⁰ or on boiling the mixture,^{87, 90a, 409} Both isomers form the same hydrochloride, a fact that is indicative of the movement of a double bond during the isomerization.^{87, 410} Phyllocladene is tetracyclic and probably contains the phenanthrene nucleus, an additional ring, and a double bond

(unlocated).^{87, 90} The isomerization of phyllocladene (dacrene) occurred also at 800-900° under one mm. Hg absolute pressure, and as a result of treatments with formic, acetic, chromic, or nitric acids.⁶⁶



Phyllocladene

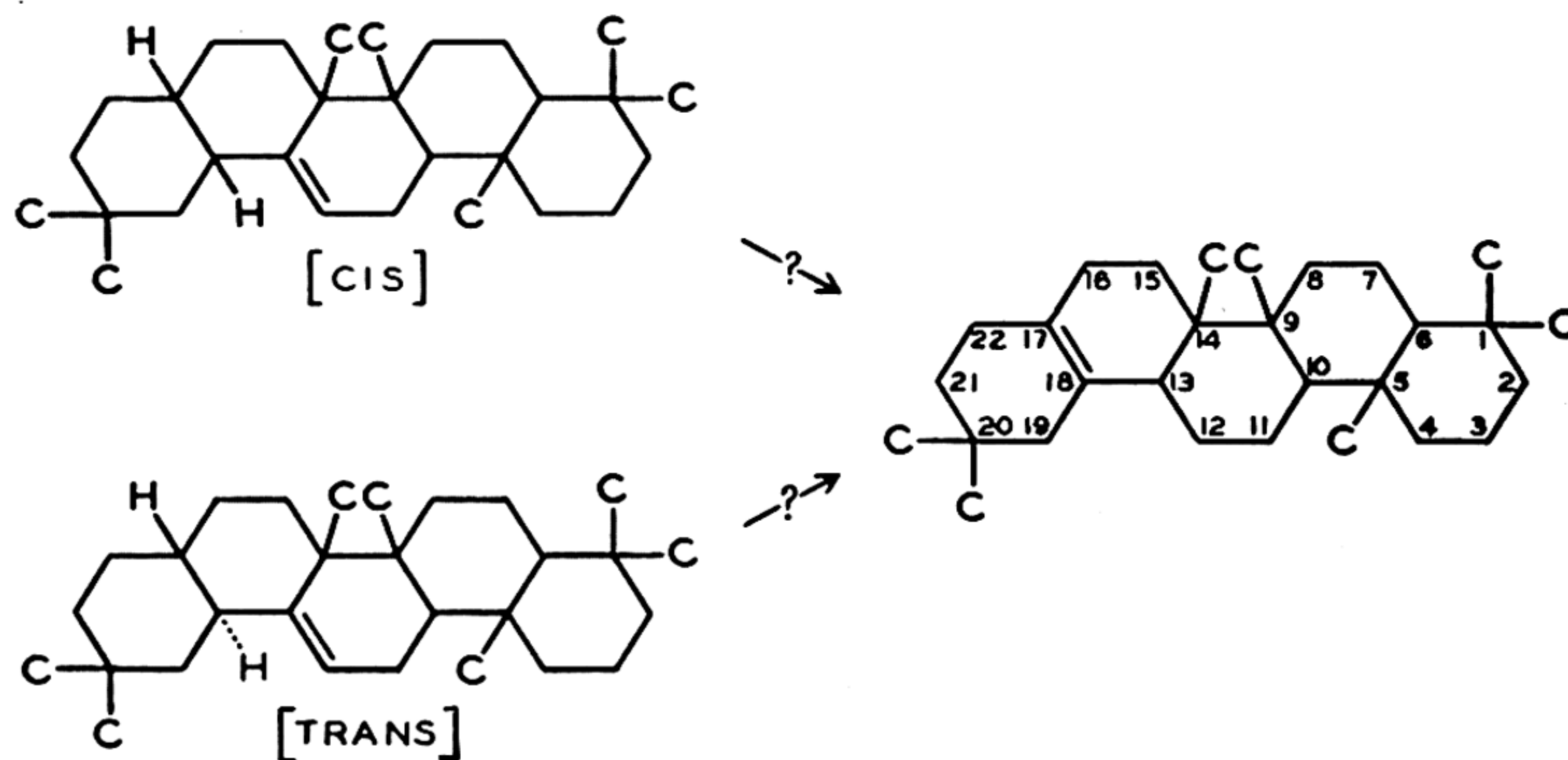
(Tentative structure based upon formulas for caryophyllene and clovene)

The isomerizations of the tetracyclenes are presented in Table 32, p. 354.

PENTACYCLENES

Isomerizations

The isomerizations of two pentacyclenes, obtainable indirectly from oleanolic and quillaic acids, have been reported recently.^{65a} *d*-17,18-*cis*- $\Delta^{12,13(?)}$ -Oleanene and *d*-17,18-*trans*- $\Delta^{12,13(?)}$ -oleanene were isomerized to $\Delta^{17,18(?)}$ -oleanene when boiled with acetic acid containing hydrochloric acid and amalgamated zinc:



The number system of oleanenes and quillaic acid is retained by the present authors in order to avoid a possibly erroneous, though more systematic, eicosahydopicene classification. Table 33 (p. 354) gives further data on the foregoing isomerizations of pentacyclenes.

Chapter VI

Aromatic Hydrocarbons

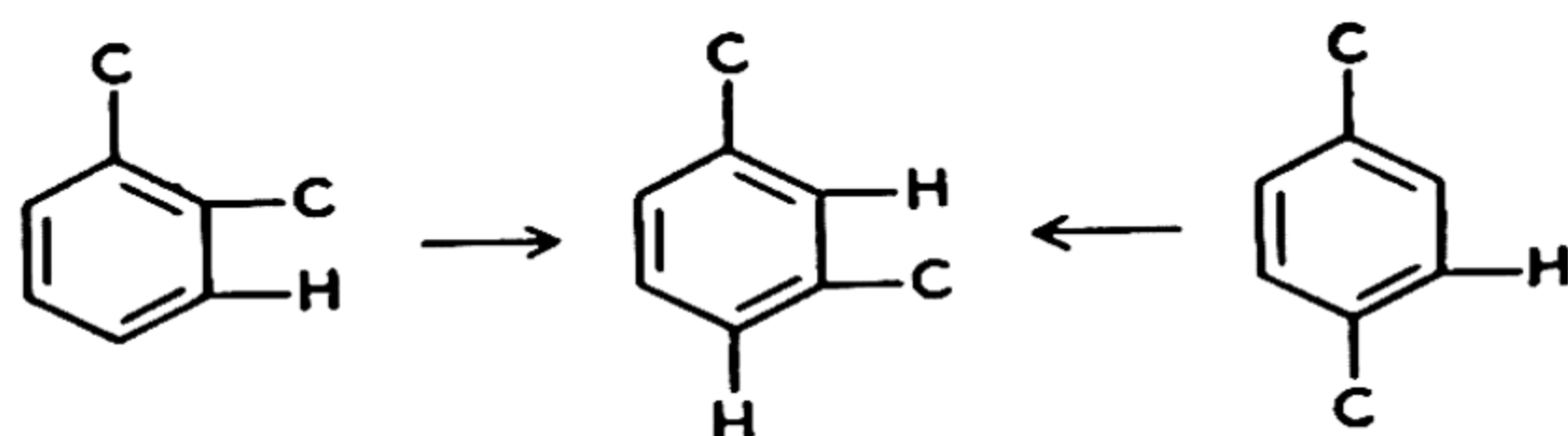
The number of observed isomerizations in the aromatics is large, though changes in the ring itself are seldom encountered. The isomerizations of aromatics observed to date can be explained generally by certain non-aromatic hydrocarbon reactions, such as hydrogen migration, formation of alkyl, alkenyl, and alkylidene radicals; intermediate-product formation; and cyclization plus decyclization. The aromatic hydrocarbons will be considered in the structural order: alkyl benzenes, alkenyl benzenes, alkadienyl benzenes, alkapolyenyl benzenes, alkynyl benzenes, indenenes, naphthalenes, anthracenes, phenanthrenes, highly-condensed aromatics, aromatic-cyclane hydrocarbons, and aromatic-cyclene hydrocarbons.

Mechanism

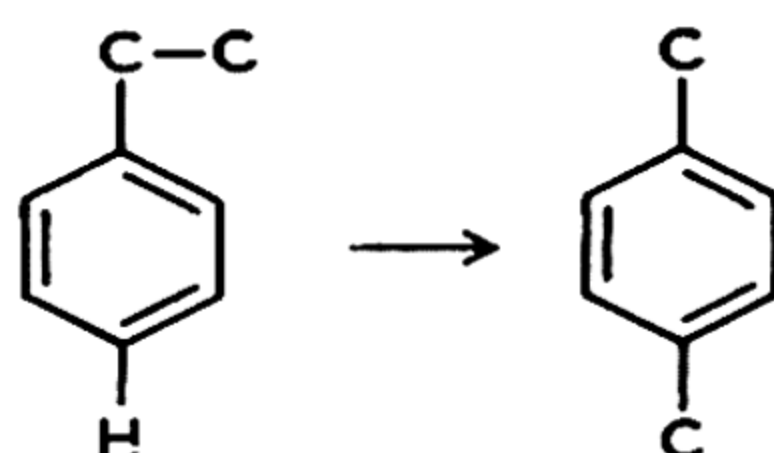
ALKYL BENZENES

The alkyl benzenes, or monocyclic aromatic hydrocarbons with saturated side-chains, can be expected to undergo several types of isomerization. Four of these types are well-known or expected instances occurring by *changes outside of the ring*:

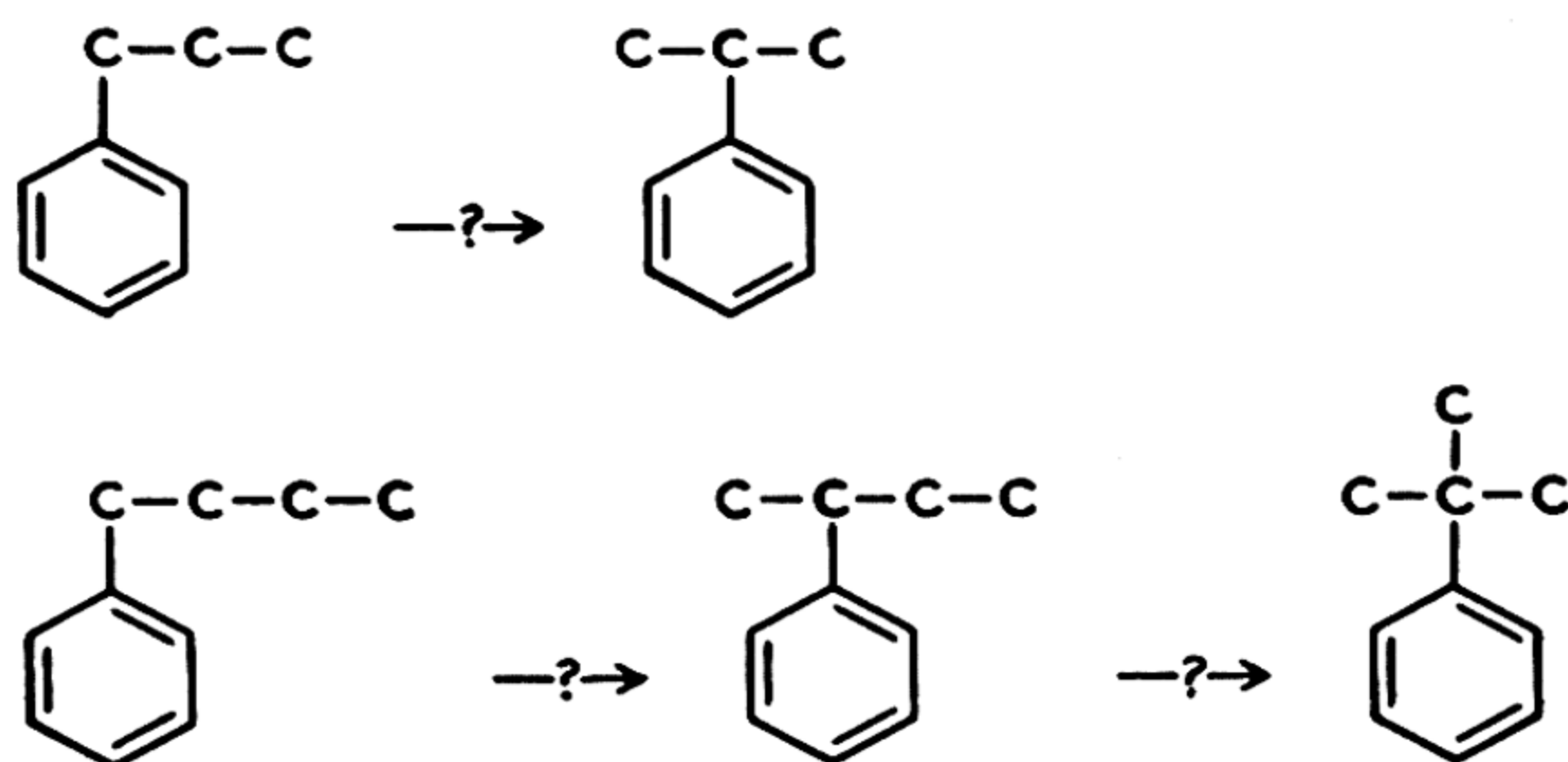
1. Isomerization by shifting of intact alkyl groups along the ring. This requires the following over-all changes: dehydrogenation (one hydrogen only) plus dealkylation, and a subsequent alkylation plus hydrogenation. An exchange in the position of alkyl and hydrogen takes place:



2. Isomerization by rupture within the side-chain, followed by a distribution of the new radical, or new radicals, along the ring. The over-all changes are dehydrogenation (one hydrogen only) at the ring plus scission within side-chain, followed by alkylation plus hydrogenation, *e.g.*:

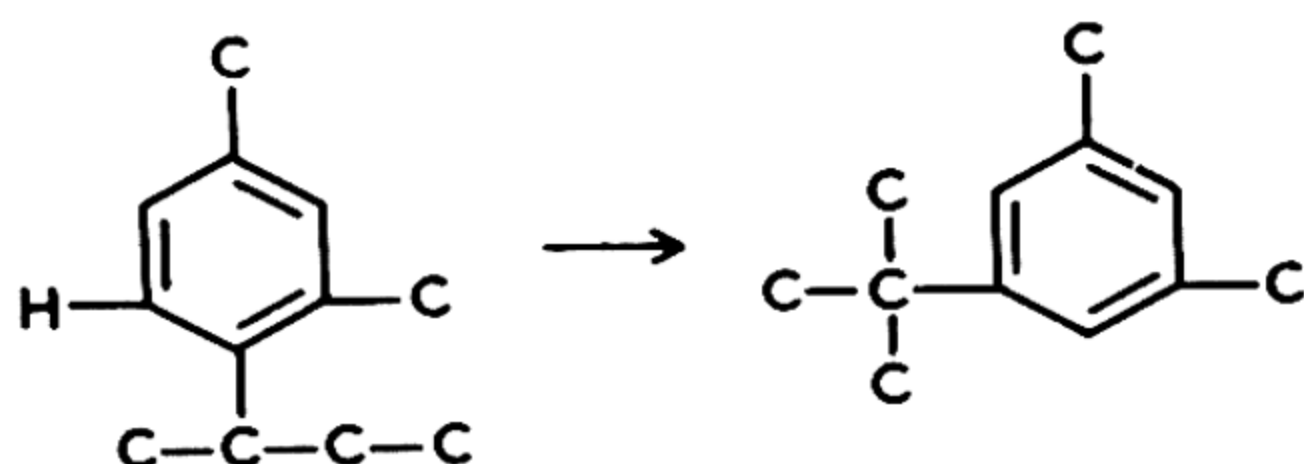


3. Isomerization within the side-chain itself, consisting of ruptures therein and the formation of a more symmetrical side-chain:



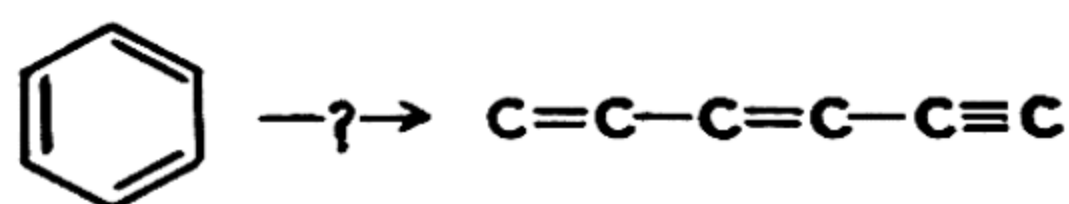
This isomerization has not been observed to date.

4. Isomerization by shifting of rearranged alkyl groups along the ring. The over-all changes required are: dehydrogenation plus dealkylation plus rearrangement of alkyl, and a subsequent alkylation plus hydrogenation. An exchange in position of the single hydrogen and new alkyl occurs. This shift can be considered a combination of types 1 and 3:

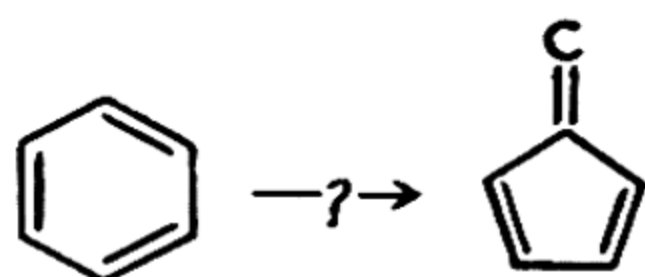


Besides these 4 types, there are 4 kinds of isomerization involving ring changes that can be expected under unusual reaction conditions. In the following types, the postulated products are still to be isolated via isomerization, although hexadien-1,3-yne-5, substituted fulvenes, and "semi-benzenes" are known.

5. Opening of the ring with the formation of extremely reactive straight-chain unsaturated hydrocarbons, for example:

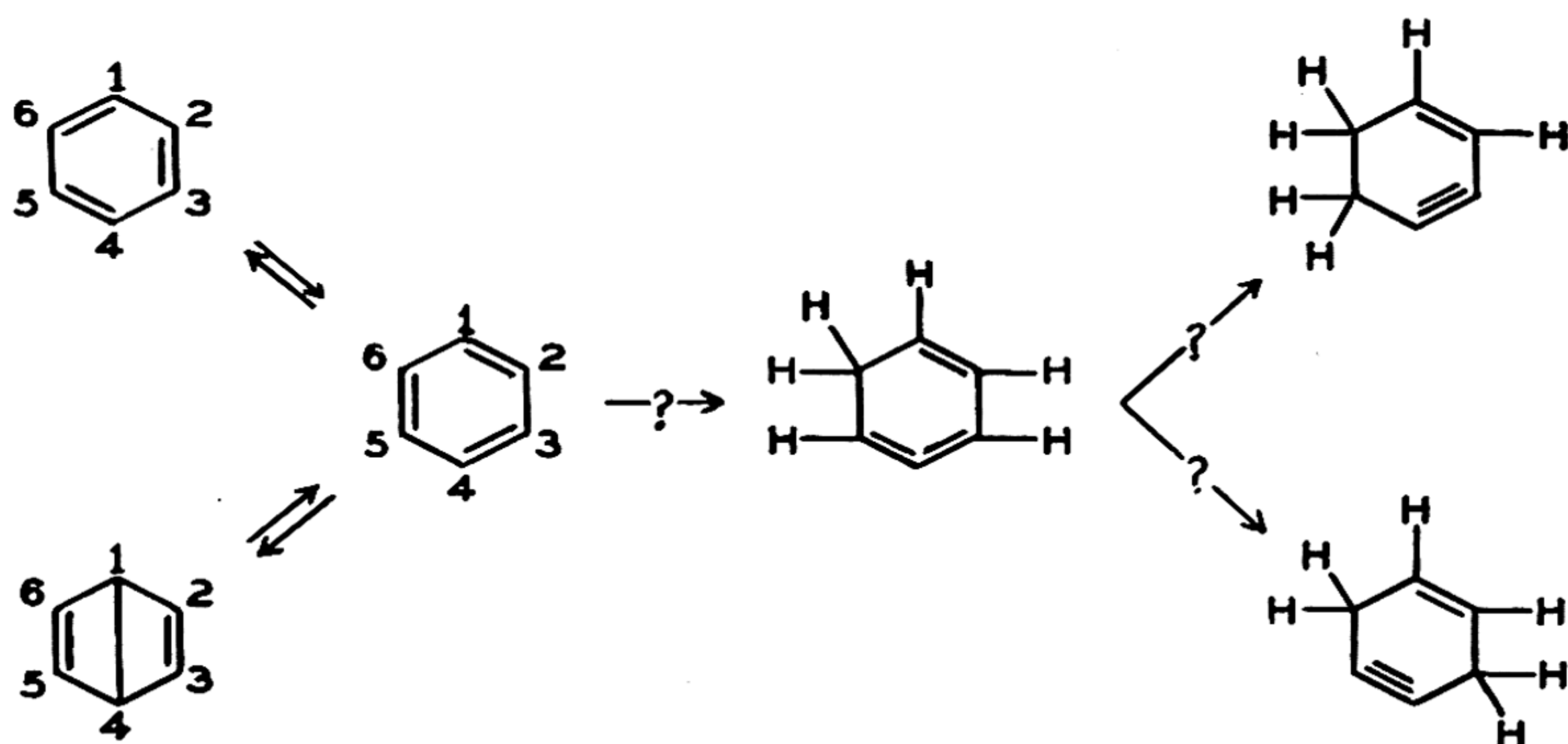


6. Opening of the ring with subsequent closure to form a reactive fulvene:

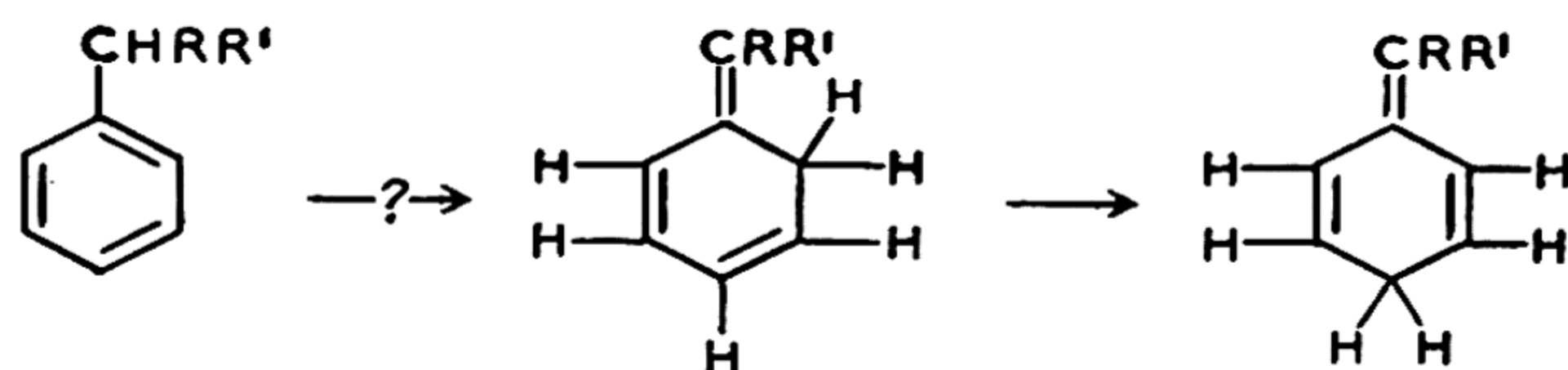


7. Changes of the type of bonds present *within the ring*, i.e., converting aromatic bonds into allenic, triple bond, and para-bond types. The

cyclic alkene-allene and cyclic alkene-alkynes seem to be ruled out for stereochemical reasons:



8. Shift of a double bond into the side-chain:



Many more hypothetical isomerizations could have been included. Only those encountered at times in the literature have been given as illustrations.

Isomerizations

There is no direct experimental evidence of isomerization according to types 5, 6, and 7. This may be due to extreme reactivity of the unsaturated products, to unfavorable states of equilibrium, or to stereochemical barriers preventing their formation. However, benzene reacting with aluminum chloride gives alkyl benzenes, showing that the ring does break up; benzene when heated at 180-200° for 48 hours with 20 per cent of aluminum chloride gave toluene and ethylbenzene.¹⁹⁶ The action of aluminum chloride (10 per cent) plus dry hydrogen chloride on benzene, at 125° for 24 hours in a closed autoclave, gave 1.7 per cent of ethylbenzene.²⁸⁰

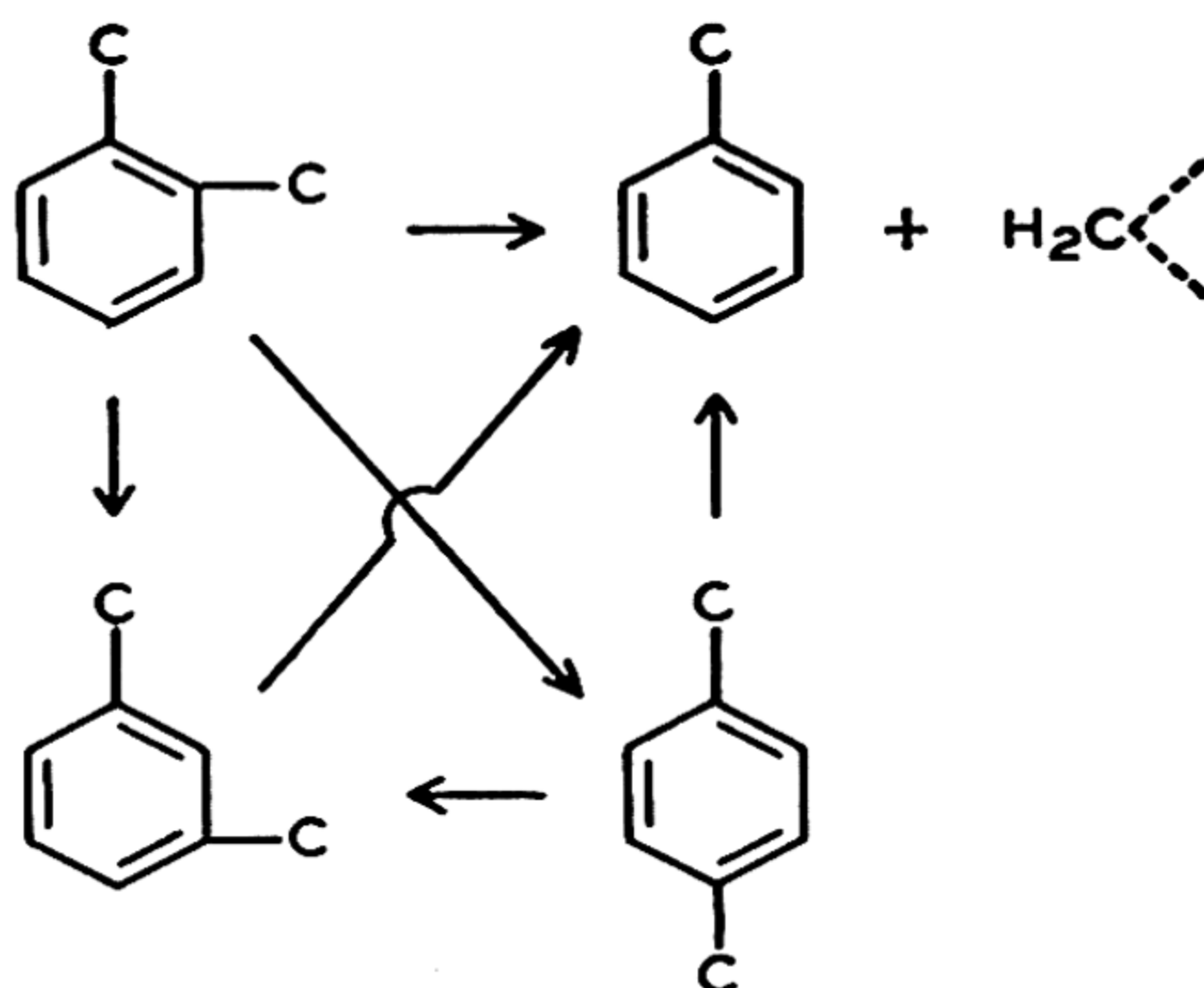
A study of the ultraviolet absorption spectrum of toluene (the simplest member of a group of toluenes corresponding to the last postulated type of isomerization) at 67° revealed the appearance of new (methylene) lines. This can be explained by the tautomerization of toluene into a form containing a double bond outside of the ring.³⁷⁶ The corresponding change of 1-methylcyclohexene-1 into methylene-cyclohexane has been considered already under the Cyclenes.

The dimethylbenzenes (xylenes) undergo isomerization by a shift of methyl groups along the ring.^{6, 7, 245, 392, 414, 415} This reaction occurred under the catalytic action of aluminum chloride plus hydrogen chloride for 10 minutes at 55°⁴¹⁴ or for 5 hours at 50°,⁴¹⁵ also for 15 minutes at 94°⁴¹⁵ or for 6 hours at 100°,²⁴⁵ producing much *m*-xylene. It has been pointed out (a) that changes in temperature affect the relative proportions in which isomers are formed from the xylenes; (b) that a decrease in the molecular ratio of aluminum chloride to xylene decreases the isomerization rate and the percentage of decomposition; and (c) that hydrogen chloride increases the decomposition without changing the relative proportions of isomers.⁴¹⁵ The effects of structure of the initial xylenes, contact time, and temperature upon the composition of the entire final product are brought out in Table 34.

Table 34. Isomerization of Xylenes by Aluminum Chloride (55.7%) in the presence of Hydrogen Chloride.⁴¹⁵

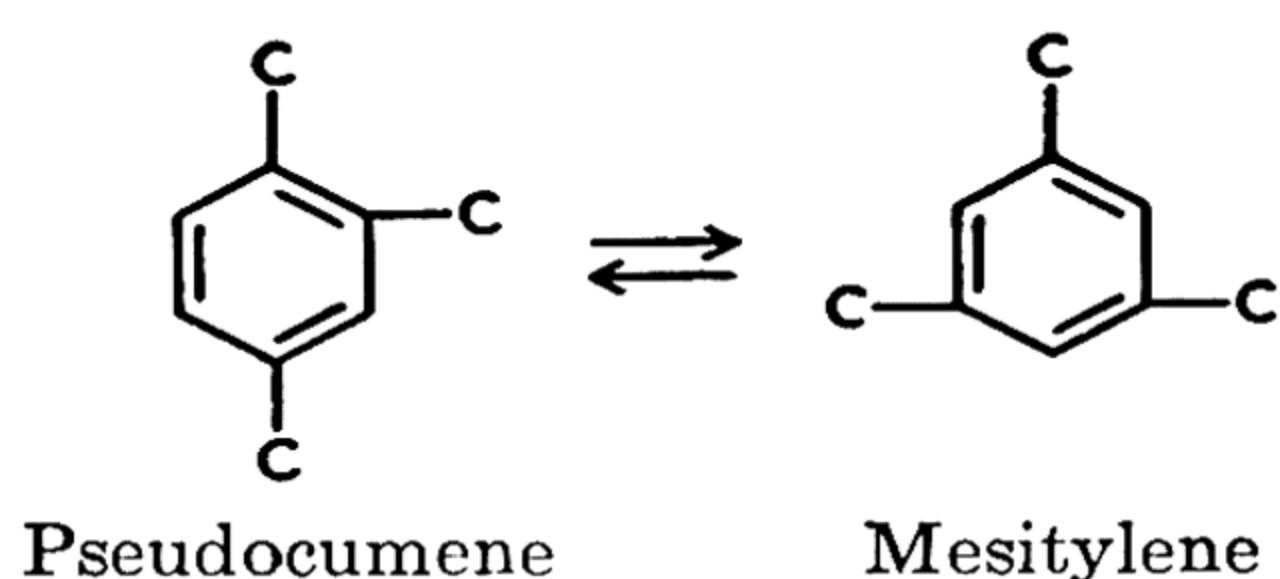
Starting Material (Reacting Xylene)	Reaction Conditions		Percentage of Products		
	Contact Time (hours)	Temp. (°C.)	<i>o</i> -Xylene	<i>m</i> -Xylene	<i>p</i> -Xylene
ortho	5	50	<37.6	<51.7	<4.7
ortho	0.25	94	<31.9	<38.6	<13.4
meta	0.5	50	0(?)	89.2(?)	2.8
meta	1.5	50	15	72.4	6.6
meta	5	50	11.7	61.9	10
meta	18	50	12.9	55.7	12.1
meta	20	50	<16	<69	<15
meta	30	50	12.5	53.9	12.1
meta	48	50	11.1	46.6	11.8
meta	50	50	<12.8	<53.6	<14.4
meta	75	50	10.2	41.7	12.2
meta	0.25	94	<18	<72	<10
para	5	50	<11.6	<63.1	<8.3
para	0.25	94	<14.4	<27.9	<47.7

In Table 34, the percentage of isomer products is given for 1:1 molar initial concentrations of xylene and aluminum chloride (in the presence of hydrogen chloride).⁴¹⁵ Complexes of aromatics with aluminum chloride (a large number of which have been described) probably play an important role in such isomerizations.^{160, 412, 414, 416} The thermal isomerization of *o*- and *p*-xylenes in a porcelain tube at 700-770° gave respectively 76.3-22.5 and 0.0 per cent of *o*-xylene, 4.0-16.8 and 1.2-4.1-3.8 (4.1 = maximum) per cent of *m*-xylene, trace-4.6 and 88.2-45.4 per cent of *p*-xylene, along with 4.6-12.8 and 2.1-13.3 per cent of toluene, 12.1-25.4 and 6.9-19.3 per cent of "condensed products," and 2.1-14.8 and 0.9-14.8 per cent of gas.¹³⁹ *m*-Xylene gave 1.7-15.4 per cent of toluene under the same conditions, but was not isomerized. *p*-Xylene gave 3.3 per cent of crude *m*-xylene when passed through a quartz tube at 800°.²⁸ It is possible that "demethylation" to toluene proceeds concurrently with, and more or less independently of, these isomerizations:

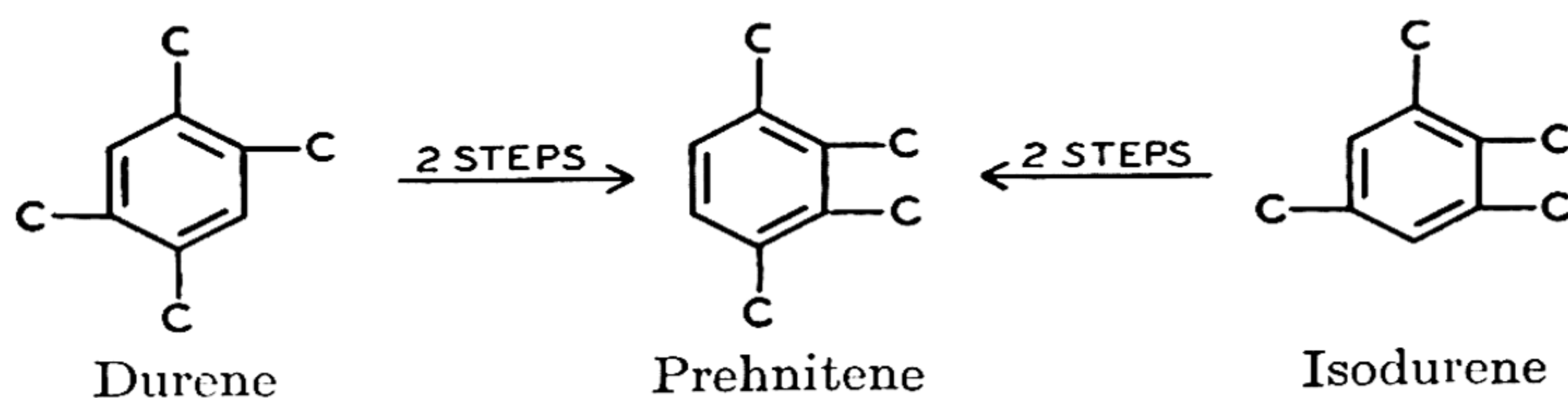


It is interesting to note the following facts concerning the stability of C_8H_{10} aromatics. *o*- and *p*-Xylenes isomerized mainly to the meta derivative, just as did the corresponding cyclohexanes. Ethylbenzene did not isomerize to xylenes in the presence of aluminum chloride at 100° or 136° .²⁴⁵ However, ethylbenzene when passed slowly through a "moderately red"-hot porcelain tube formed styrene and smaller amounts of benzene, toluene, *p*-xylene, and naphthalene.^{61, 63} The observed small amount of *p*-xylene may be due to secondary reactions, but when considered together with other findings, it warrants an investigation of the stability of the ethyl group at the center of the chain.

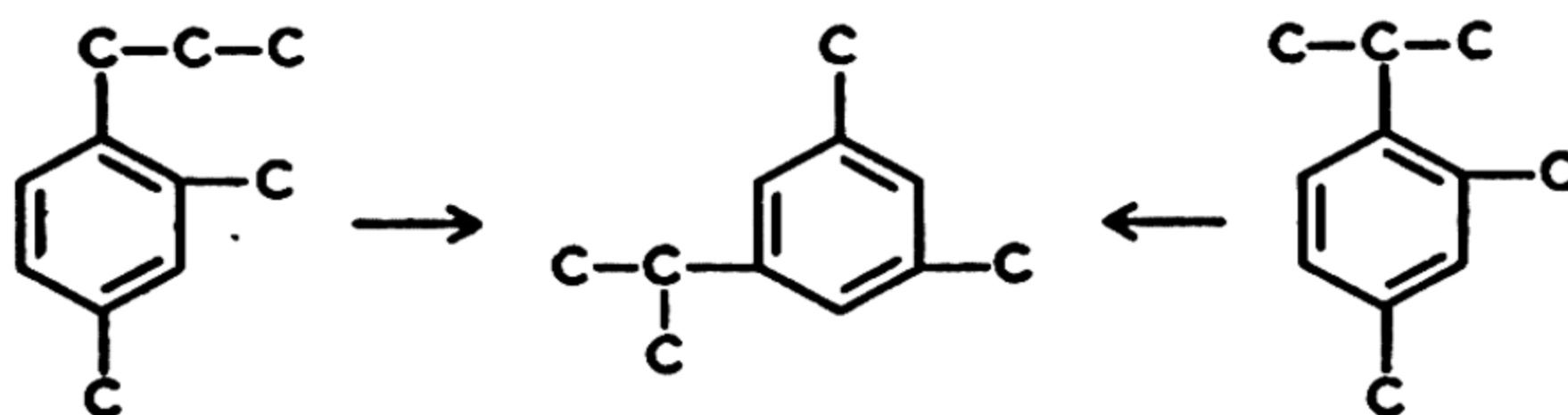
The polyalkyl aromatics also show the first type of isomerization. 1,2,4-Trimethylbenzene (pseudocumene), in the presence of aluminum chloride at 150 - 160° , gave 1,3,5-trimethylbenzene (mesitylene), and vice versa:²⁹⁰



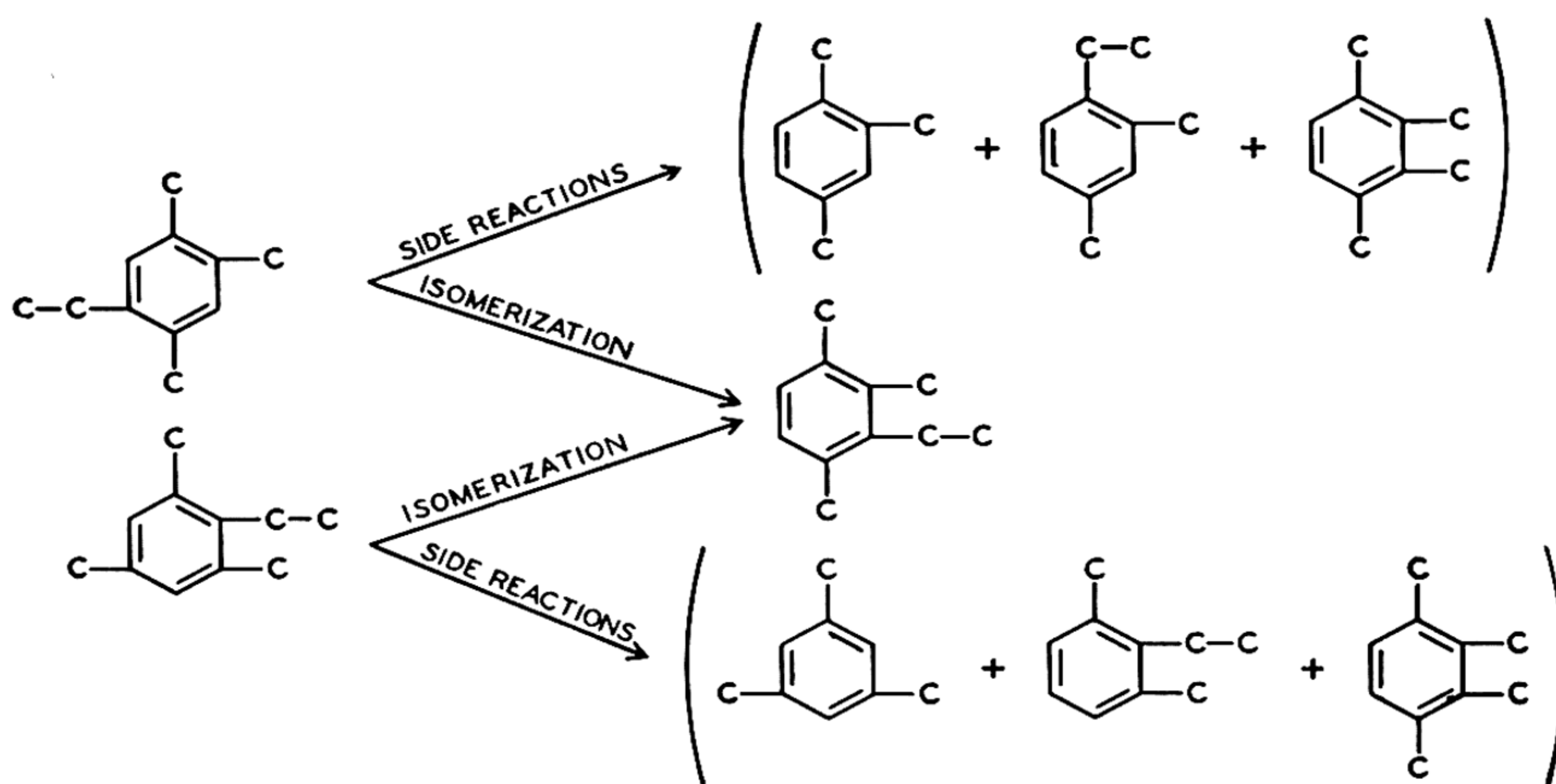
1,2,4,5-Tetramethylbenzene (durene) and 1,2,3,5-tetramethylbenzene (isodurene) formed 1,2,3,4-tetramethylbenzene (prehnitene) when sulfonated in the presence of sulfuric acid and subsequently hydrolyzed.⁵⁵⁸ A flash system of hydrolysis (at 140 - 150°) by dilute sulfuric acid and superheated steam was utilized:⁵⁶⁰



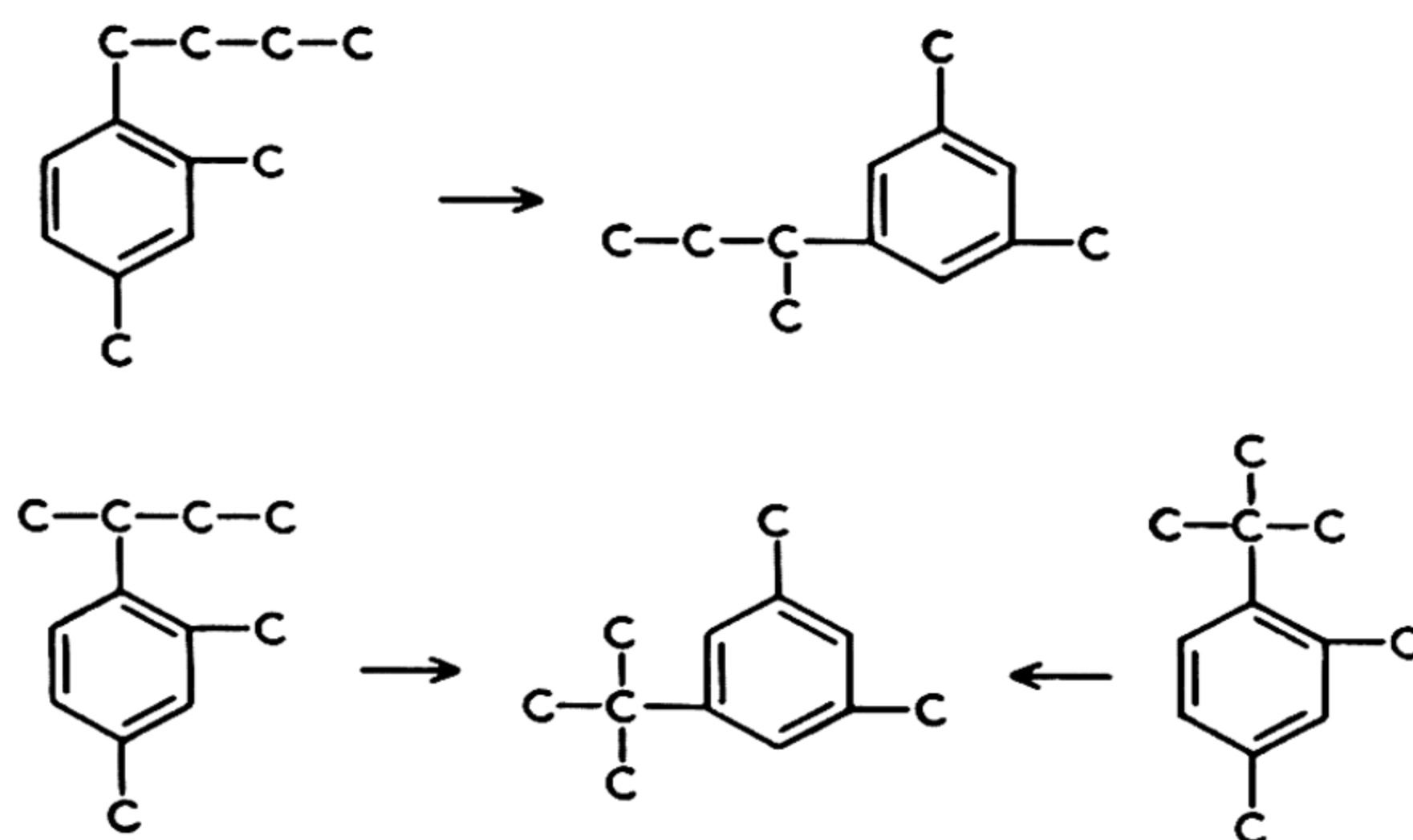
The treatment of 1-*n*-propyl-2,4-dimethylbenzene (*i.e.*, "1,3-dimethyl-4-*n*-propylbenzene") and of "1,3-dimethyl-4-isopropylbenzene" with aluminum chloride at 100° and 55-60°, respectively, yielded 1,3-dimethyl-5-isopropylbenzene:⁴⁰⁴



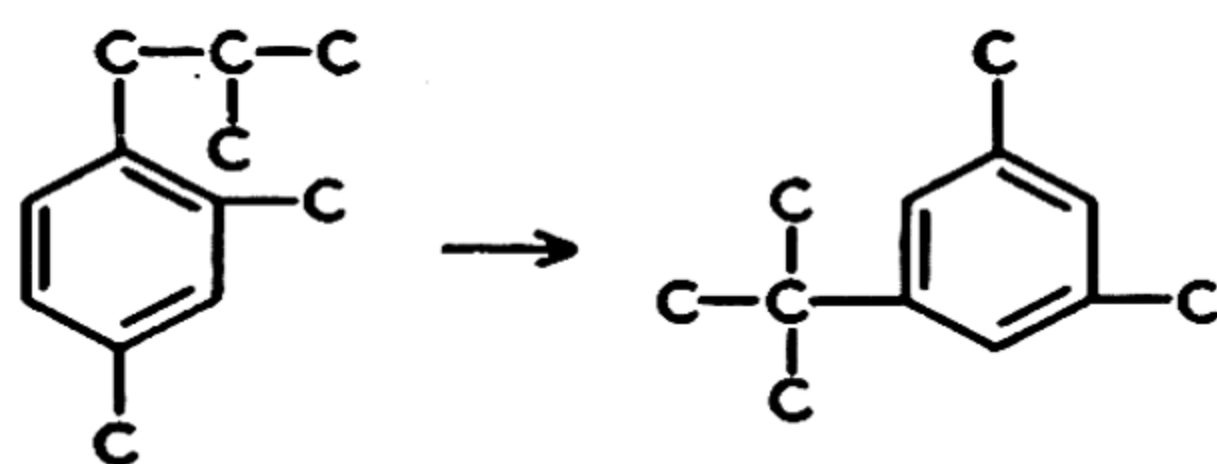
1,2,4-Trimethyl-5-ethylbenzene and 1,3,5-trimethyl-2-ethylbenzene isomerized respectively to 27.0 and 34.5 per cent of 1,2,4-trimethyl-3-ethylbenzene when subjected to sulfonation at 60-70° and desulfonation at 140-150°. ⁵⁵⁹ The isomerizations are accompanied by side reactions:



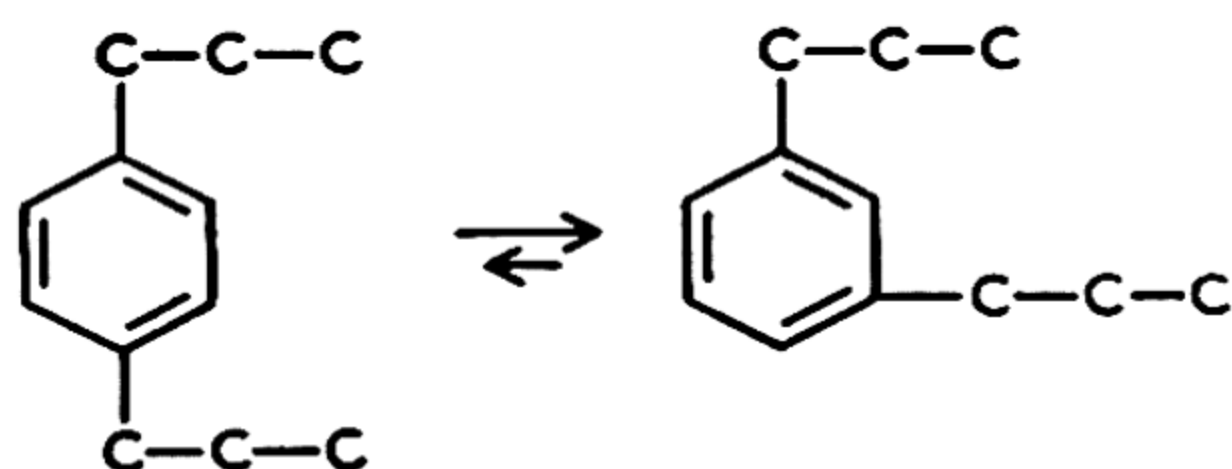
1-*n*-Butyl-2,4-dimethylbenzene (*i.e.*, "1,3-dimethyl-4-*n*-butylbenzene") gave 1,3-dimethyl-5-*sec*-butylbenzene when warmed with aluminum chloride, whereas the heating of either "1,3-dimethyl-4-*sec*-butylbenzene" or "1,3-dimethyl-4-*tert*-butylbenzene" with aluminum chloride resulted in the formation of 1,3-dimethyl-5-*tert*-butylbenzene:⁴⁰⁵



About 10 per cent of *m*-xylene was formed also, along with high-boiling (higher-alkylated?) hydrocarbons. A 45 per cent yield of 1,3,5-isomer from "1,3-dimethyl-4-*tert*-butylbenzene" has been reported;⁵⁶¹ whereas the yields of 1,3,5 isomers from the "1,3-dimethyl-4-butylated benzenes" varied from 20-60 per cent.⁴⁰⁵ "1,3-Dimethyl-4-isobutyl benzene," treated similarly with aluminum chloride, gave a "mixture" of hydrocarbons.⁴⁰⁵ Ferric chloride is a better catalyst than aluminum chloride for isomerizations of the "1,3-dimethyl-4-butylated benzenes."^{405a} The treatment of "1,3-dimethyl-4-isobutylbenzene" with anhydrous ferric chloride for 2.25 hours at 80-110° gave about 52 per cent of 1,3-dimethyl-5-*tert*-butylbenzene:

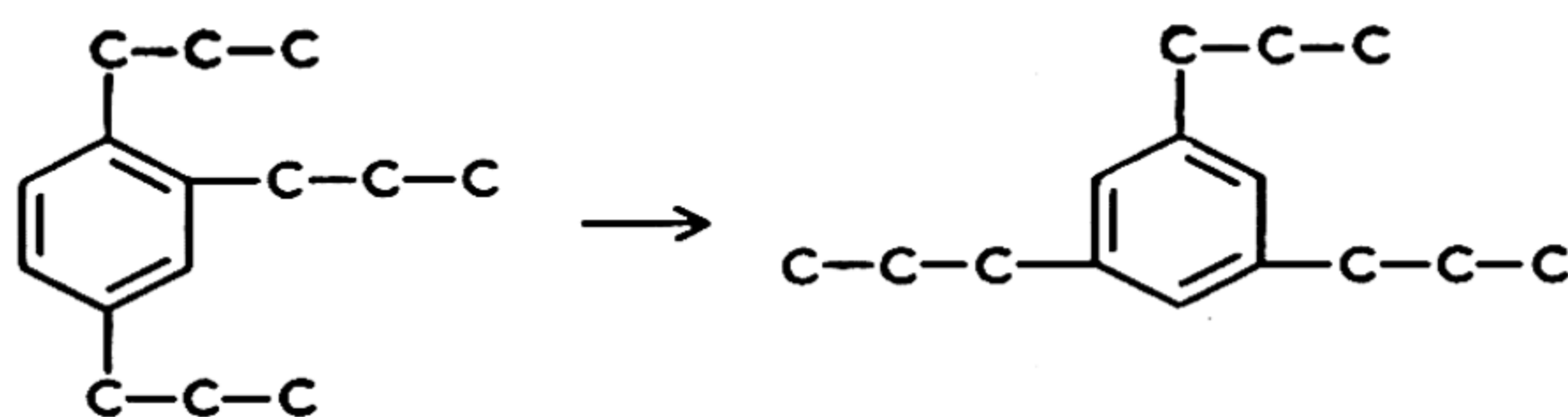


In isomerizations with aluminum chloride at 100°, *p*-dipropylbenzene yielded 66.7 per cent of *m*-dipropylbenzene in 2 hours (dropping to 15.7 per cent in 22 hours), whereas *m*-dipropylbenzene formed only a small amount of the para compound when similarly treated for 22 hours:²⁷



1,2,3,5-Tetraethylbenzene and 1,2,4,5-tetraethylbenzene were converted into 1,2,3,4-tetraethylbenzene by sulfonation with sulfuric acid at 100°, followed by hydrolysis at 130-150° in the presence of "50 per cent sulfuric acid" and steam.^{558a} These indirect isomerizations are analogous to those of isodurene and durene, which form prehnitene, but the present yields are considerably higher (over 85 per cent).

1,2,4-Tripropylbenzene formed 28 per cent of 1,3,5-tripropylbenzene when treated with aluminum chloride for 4 hours at 100°:²⁷

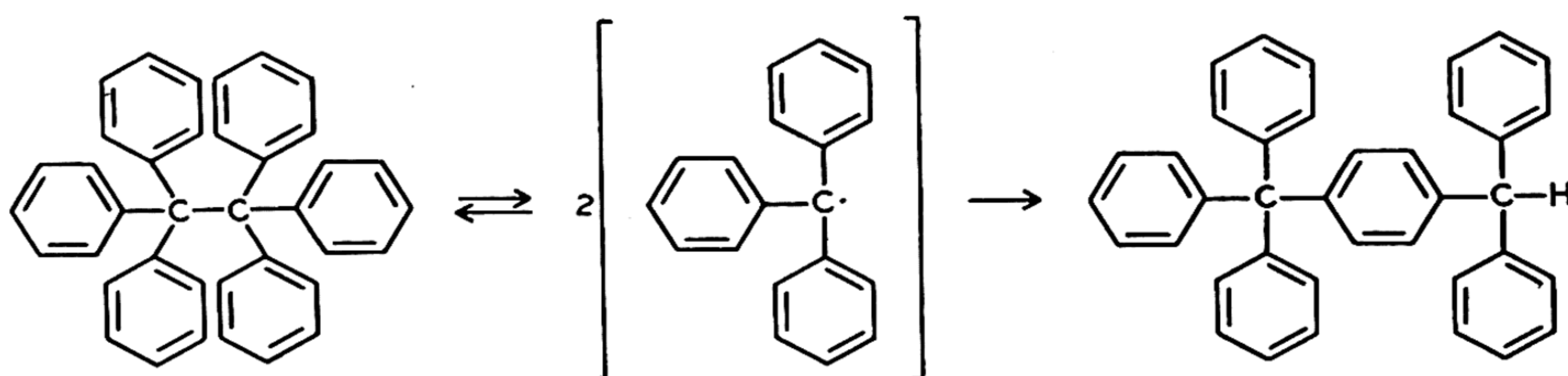


Some doubt⁴⁰⁵ has been expressed about the "normal character" of the migrating propyl group, since isopropyl groups would be formed by a

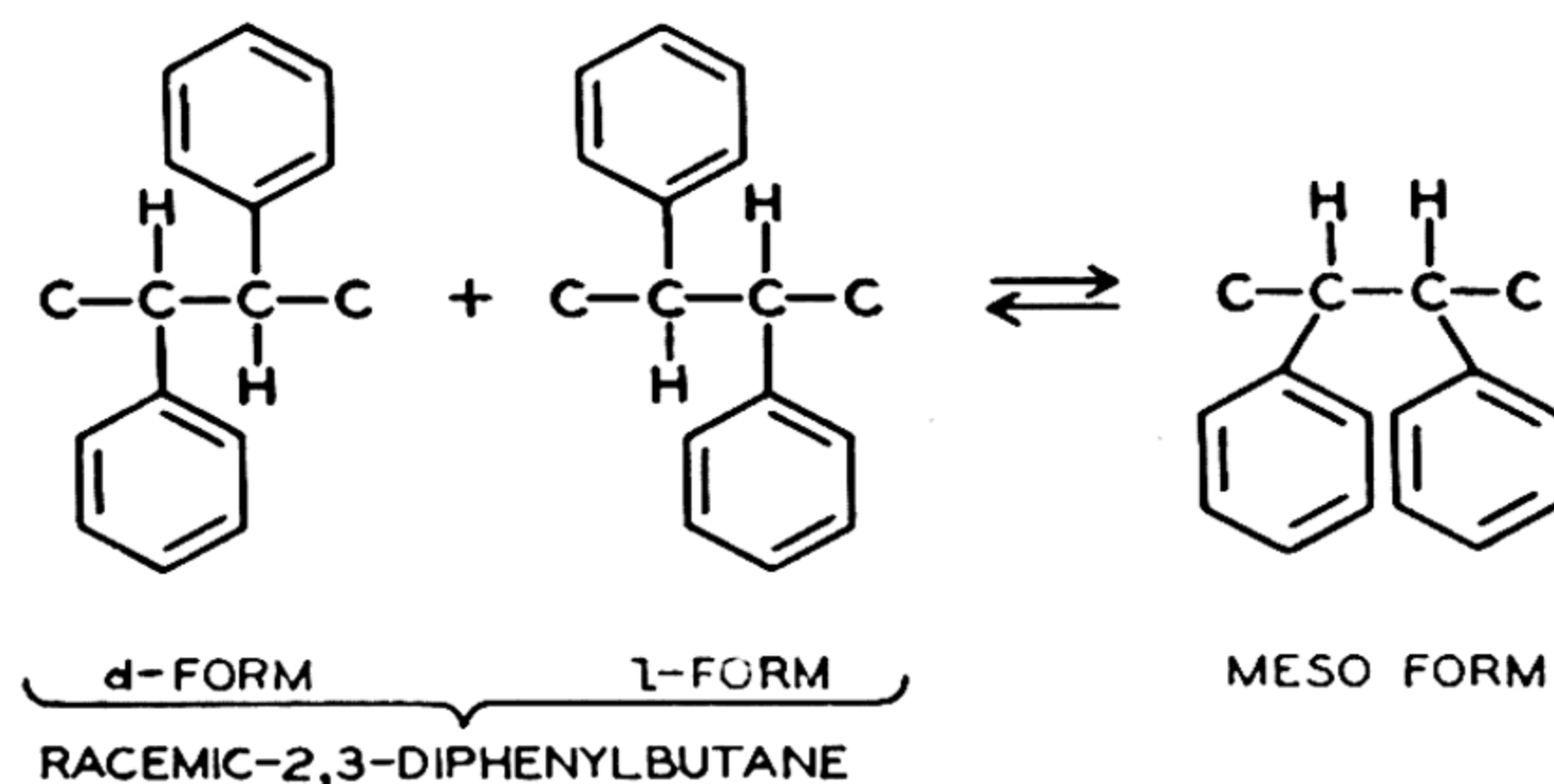
side-chain isomerization. The foregoing isomerizations²⁷ were accompanied by the formation of lower- and higher-propylated products, which represents drastic reaction conditions for an intact migration of *n*-propyl groups.

Triphenylmethane has been described as occurring in stable (m.p. 92°) and unstable (m.p. 81°) forms,²⁰⁷ as well as in a labile form (m.p. 92.5°, uncorrected).²³³ The labile form, when heated at 75-80°, gives the stable form (m.p. 92.5°, uncorrected), but it is very uncertain whether an isomerization of triphenylmethane takes place.

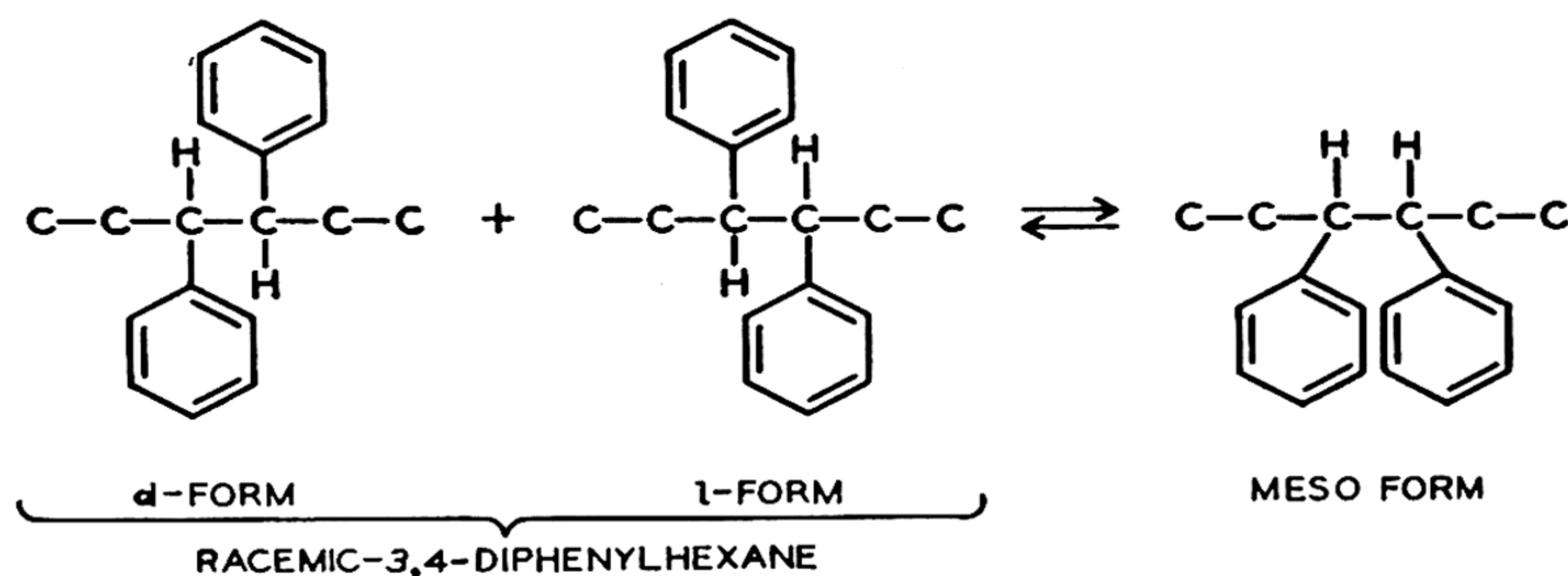
Hexaphenylethane^{223, 593} is another example of an aromatic containing several phenyl groups. It has been isomerized into *p*-benzohydryl-tetraphenylmethane by (a) treatment (in benzene solution) with small amounts of hydrogen chloride gas²²² or hydrochloric acid,²²² by (b) heating with *m*-xylene,⁶⁴⁶ and by (c) treating the ether solution of "triphenylmethyl" with sodium.⁵¹⁹ The formation of *p*-benzohydryl-tetraphenylmethane involves the formation, isomerization, and recombination of intermediary free radicals:



2,3-Diphenylbutane is known in a liquid (*dl*) and in a solid (meso) form; the liquid form is converted into the latter when heated at 235-250° for 8 hours:³³⁴



3,4-Diphenylhexane exists in a liquid (*dl*) and in a solid (meso) form, partly convertible into each other by heating with iodine at 250-265° in a sealed tube:³³⁵



Isomerizations of alkyl benzenes are listed in Table 35, p. 356.

Conclusions

1. Reactions of types 1 (shift of intact alkyl groups), 2 (new alkyls via rupture within side-chains), and 4 (shift of rearranged alkyl groups) are accompanied by the formation of lower- and higher-alkylated aromatics, which indicates a complete rupture of some side-chains from the initial hydrocarbons. This favors also a complete rupture in the "event" of isomerization. The detached groups may react with the ring as free radicals, or as alkenes causing alkylation (especially where the side-chains undergo an isomerization).

2. The conversion of racemic diphenyl alkanes into meso forms is an isomerization that should find numerous analogies. In fact, all monophenyl alkanes, in which a suitable alkyl replaces one of the phenyl groups of such diphenyl alkanes, may undergo this isomerization.

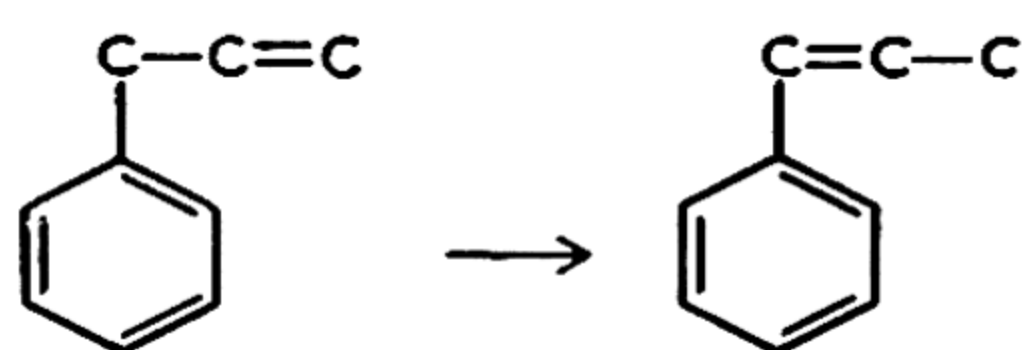
3. Recombination, rather than isomerization, of aromatic free radicals has been studied; formation of free radicals from the highly arylated ethanes is a very general reaction.

Mechanism

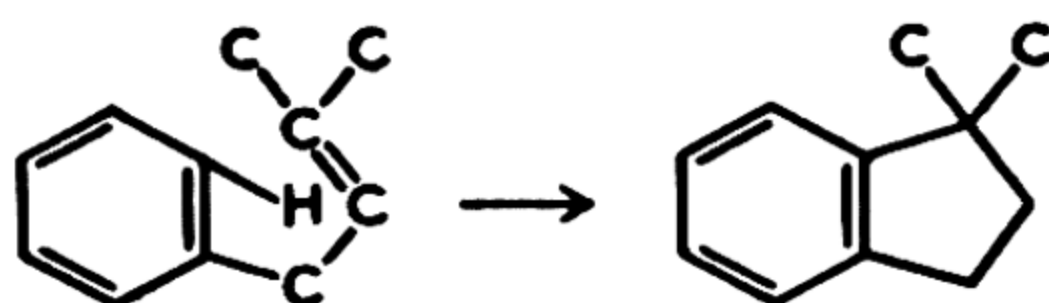
ALKENYL BENZENES

The alkenyl benzenes, or monocyclic aromatic hydrocarbons with alkenyl side-chains, can be expected to undergo more complex isomerizations than those observed in the case of alkyl benzenes. The following types of changes are often encountered:

1. Shifting of double bonds within the side-chain:



2. Cyclization, or "internal alkylation," by closure upon an unsaturated side-chain:



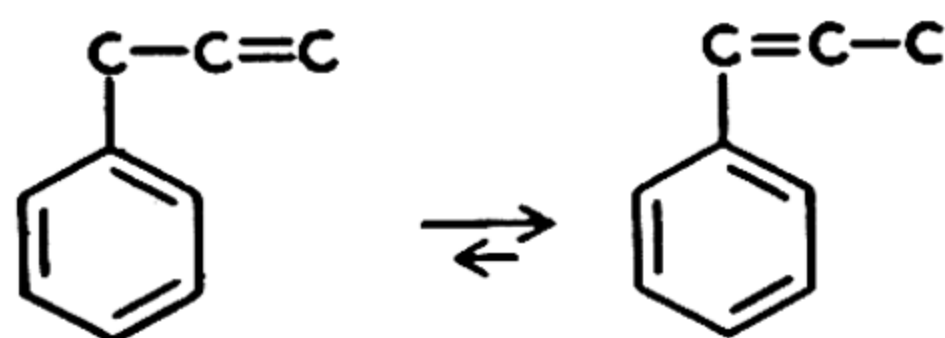
3. *Cis-trans* isomerization in unsaturated side-chains.

The isomerizations effected by changes within unsaturated side-chains attached to benzene are reactions that are characteristic of the alkenes. These isomerizations take place on heating, or by the use of various catalysts.

Isomerizations

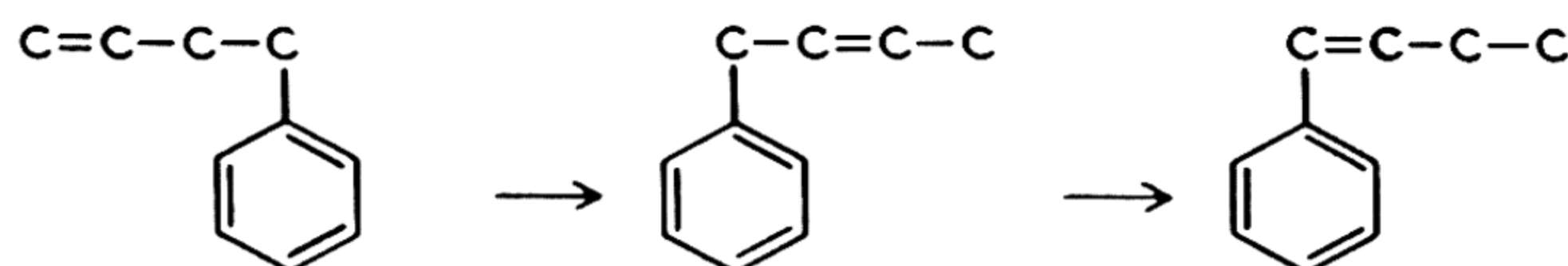
The alkenyl benzenes discussed in this section are arranged in order of increasing size of side-chain. Phenylated alkenyl benzenes are also considered at this point, because their isomerizations are related to those of the alkenyl benzenes.

Allylbenzene gave propenylbenzene when heated in the presence of dry caustic alkalies,² alcoholic potash,^{309, 584} chromia or ferric oxide at 220°, ³³⁹ alumina at 220-225°, ³³⁸ palladium at 300°, ³⁴⁸ charcoal, silica gel, or clay at 300°, ³³⁹ nickel on asbestos at 360°, ³³⁸ or infusorial earth at 500°. ^{456, 457} The reaction with dry caustic alkali is reversible:²

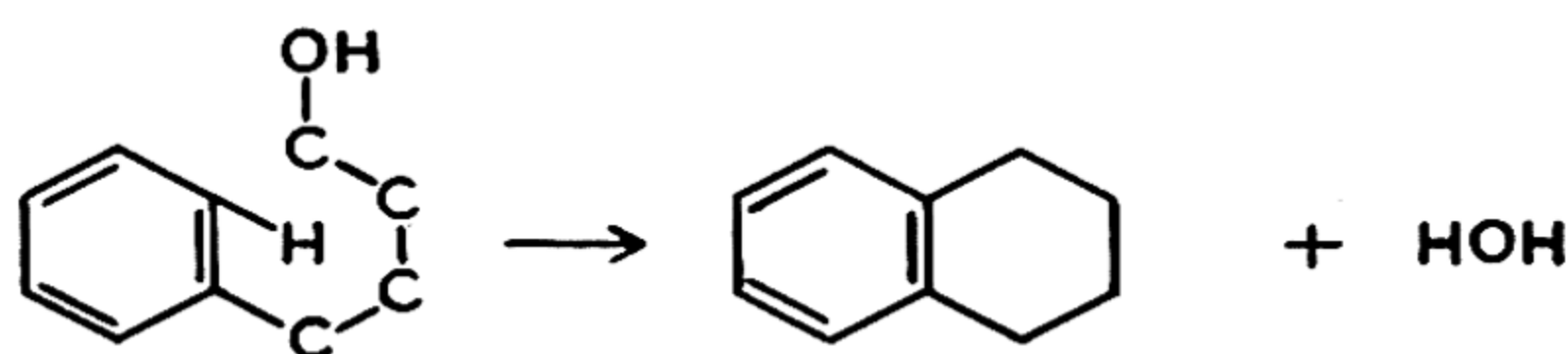


Obviously, no single mechanism can explain the formation of propenylbenzene under the various reaction conditions. The isomerization bears a similarity to that of the thermal conversion of allylcyclohexane into propenylcyclohexane.

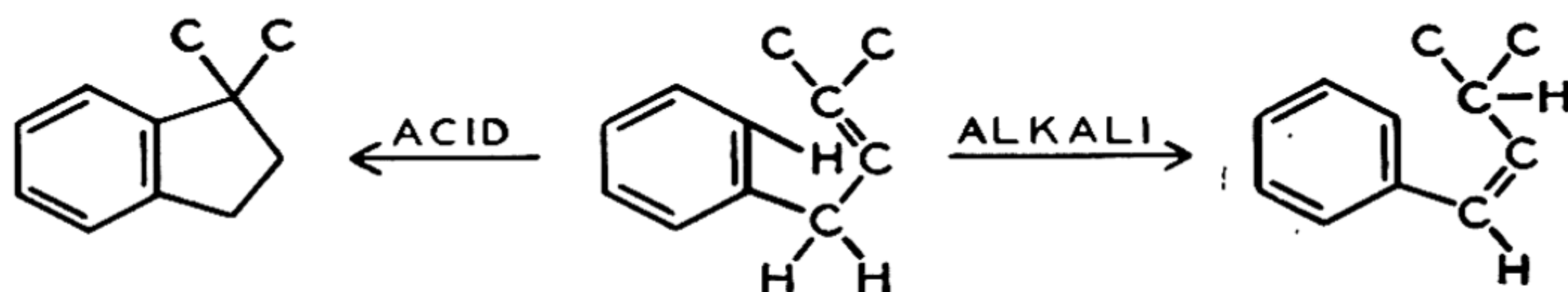
4-Phenylbutene-1 probably isomerized into a small amount of 1-phenylbutene-1 and 1-phenylbutene-2, when passed with carbon dioxide through a "Pyrex" tube at 550°. ^{261, 262} Passage of 4-phenylbutene-1 (with carbon dioxide) over platinum at 300° yielded these products. ³⁴⁵ 4-Phenylbutene-1 formed a catalyzate with 80-93 per cent of 1-phenylbutene-1 when conducted over alumina at 225-300° in a stream of carbon dioxide. ^{346a} The last workers found chromia to be a suitable catalyst at 225-250° for the same reaction and pointed out the conjugation of the product's side-chain and ring double bonds. The side-chain double bond probably migrates stepwise toward the ring:



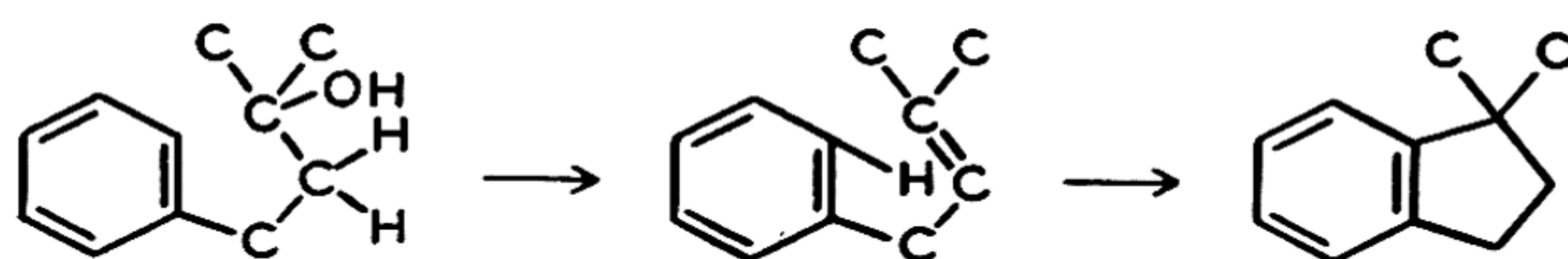
This interpretation of the reaction is substantiated by the formation of 1-phenylbutene-1 when 1-phenylbutene-2 is either boiled with alcoholic potash,¹⁸³ or heated at 160-180° with it in a bomb for a long time.³⁰⁸ Attempts⁷² to cyclize 4-phenylbutene-1 with the aid of acidic catalysts were unsuccessful, owing to the development of polymerization or other side reactions. Moreover, the cyclodehydration of 4-phenylbutanol using 85-per cent phosphoric acid, which gives the desired tetrahydronaphthalene, appears to be only a simple dehydration:⁷²



1-Phenyl-3-methylbutene-2 underwent cyclization to 1,1-dimethylindane when treated with strong sulfuric acid or 85-per cent phosphoric acid.⁷² This is an isomerization of an alkene-aromatic by an intramolecular alkylation. It proceeds mainly on account of the alkene-like properties of the initial hydrocarbon. 1-Phenyl-3-methylbutene-2, when heated at 180° with alcoholic potash, gave 1-phenyl-3-methylbutene-1.³⁰⁸ Under the opposing conditions caused by the presence of acid or alkali, the transfer of the labile hydrogen atoms of 1-phenyl-3-methylbutene-2 is highly selective:

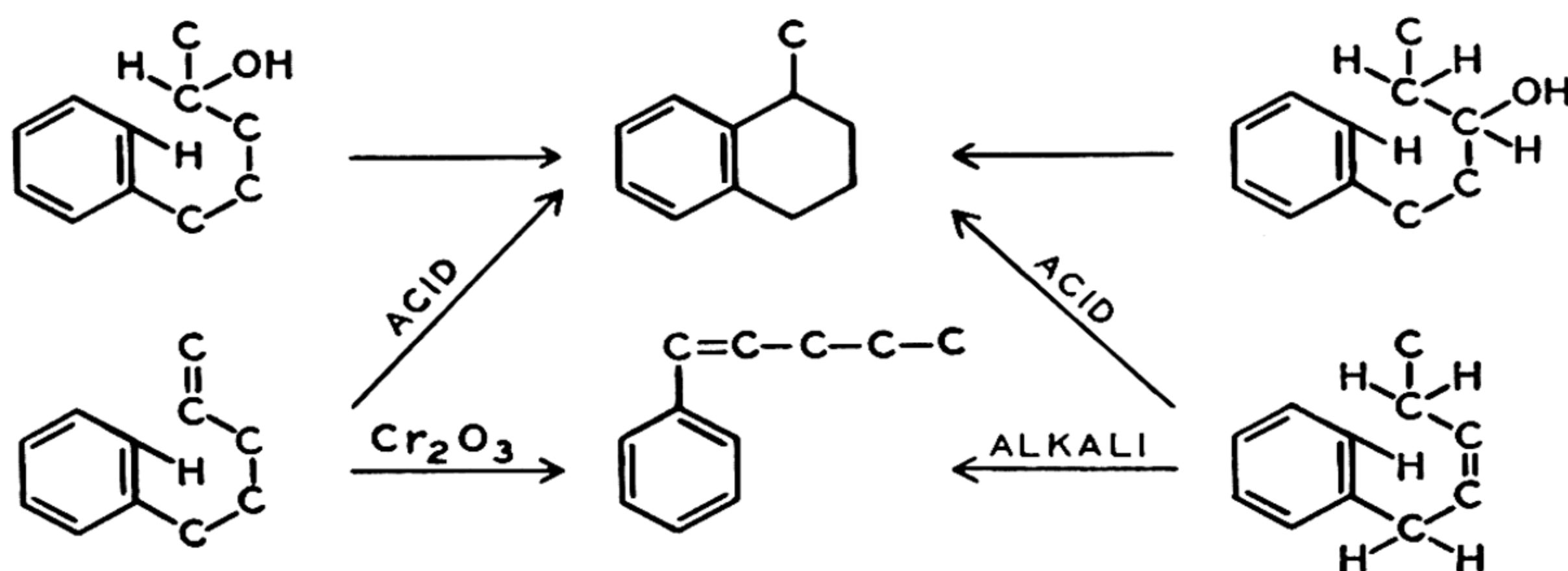


The cyclodehydration of aromatic alcohols in some cases appears to involve the intermediary formation of alkenes. The latter subsequently undergo a cyclization of the type exhibited by 1-phenyl-3-methylbutene-2, but probably polymerize also.⁷² Dimethylphenethylcarbinol, upon treatment with hot 85-per cent phosphoric acid, definitely undergoes a cyclodehydration via isomerization as follows:

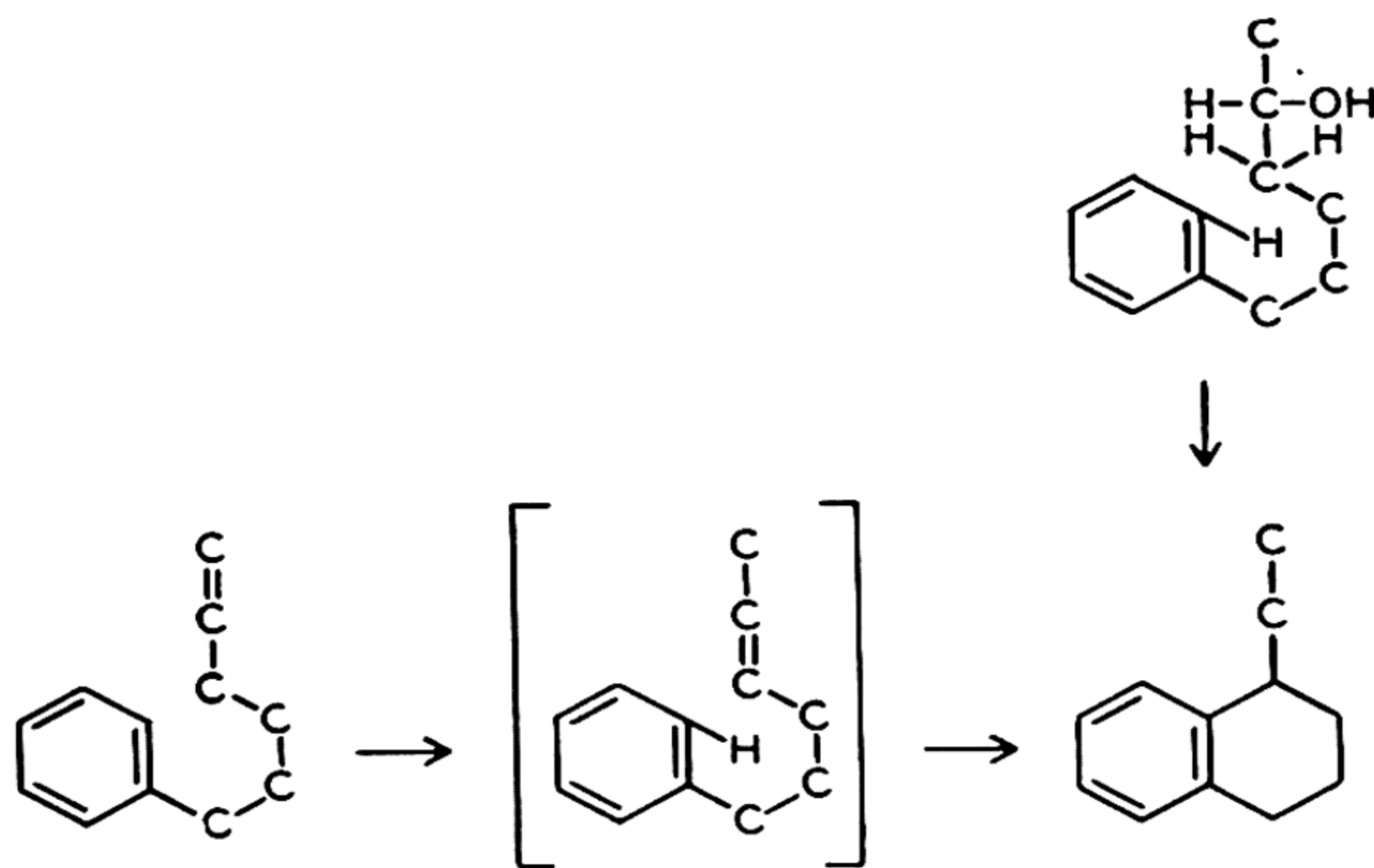


Studies⁷³ of the tetralin group have revealed that 1-methyltetralin can be obtained by cyclization of methylphenpropylcarbinol, 5-phenylpentene-1, ethylphenethylcarbinol, or 1-phenylpentene-2, using sulfuric acid. The action of 90-per cent sulfuric acid on 5-phenylpentene-1 gave

1-methyltetralin.⁴⁷¹ The isomerization of 1-phenylpentene-2 involves both cyclization and the migration of the double bond in a side-chain. Passage of 5-phenylpentene-1 (with carbon dioxide) over chromia at 250° yielded 1-phenylpentene-1, indicating a tendency toward conjugation of the ring and side-chain double bonds.^{346a} In another instance, 1-phenylpentene-1 resulted when 1-phenylpentene-2 was heated at 150° with alcoholic potash.³⁰⁹ It should be observed that here too the transfer of the labile hydrogen atoms is selective under the opposing roles assignable to acid and alkali:



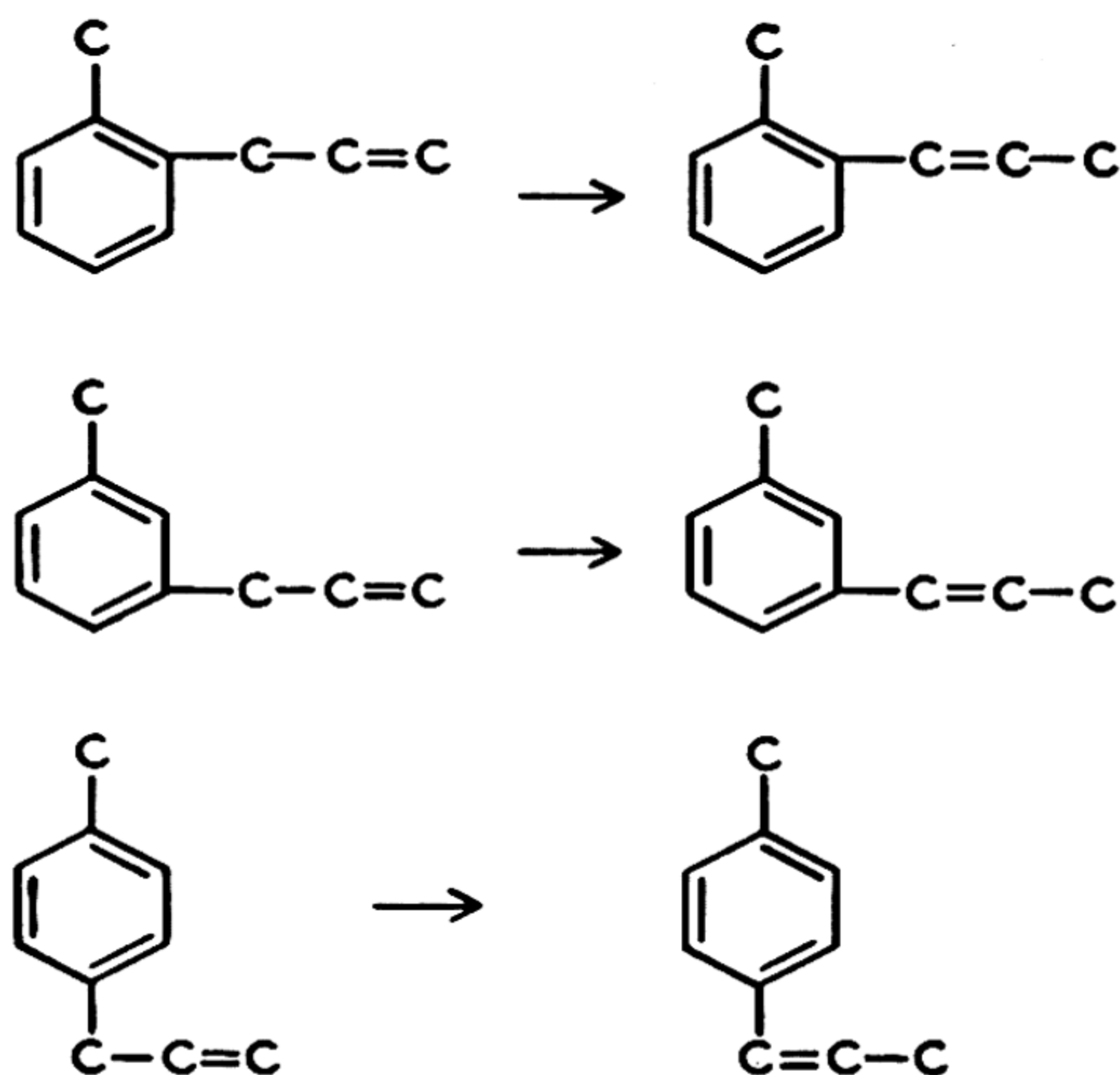
Similarly 1-ethyltetralin was prepared by the cyclization of either methylphenbutylcarbinol or 6-phenylhexene-1.⁷³ In the latter case, a shift in the location of the double bond is required, corresponding to the formation of either 6-phenylhexene-2 or 6-phenylhexene-3:



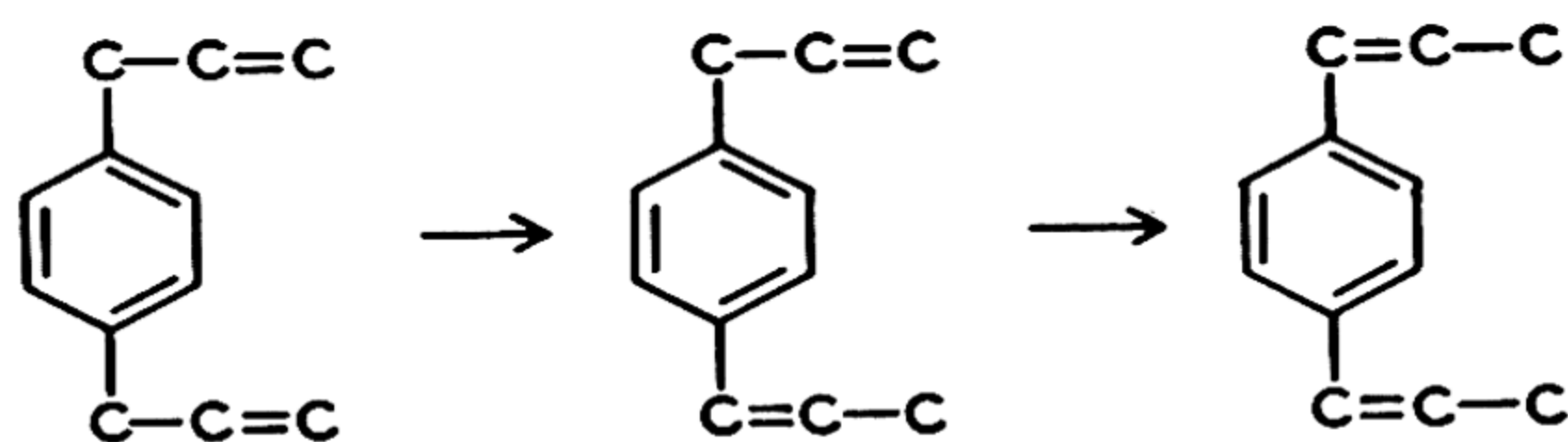
1-Ethyltetralin, for example, was prepared by the action of 90-per cent sulfuric acid on 6-phenylhexene-1.⁴⁷¹

o-, *m*-, and *p*-Allyltoluenes, passed with carbon dioxide over alumina at 220-225°, were converted quantitatively into the corresponding *o*-, *m*-,

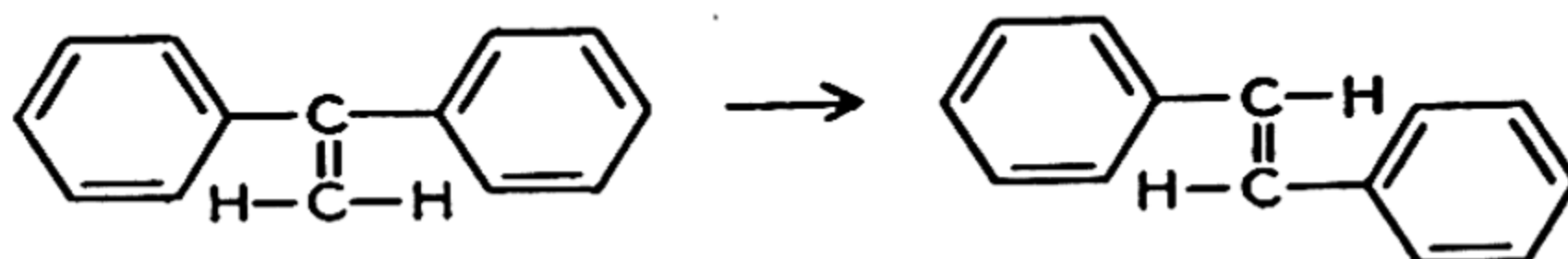
and *p*-propenyltoluenes.³³⁸ *p*-Allyltoluene, passed with carbon dioxide over platinum (30 per cent) on charcoal at 300°, was converted into 84 per cent of *p*-propenyltoluene.³⁴⁵ These isomerizations are illustrated by the following equations:



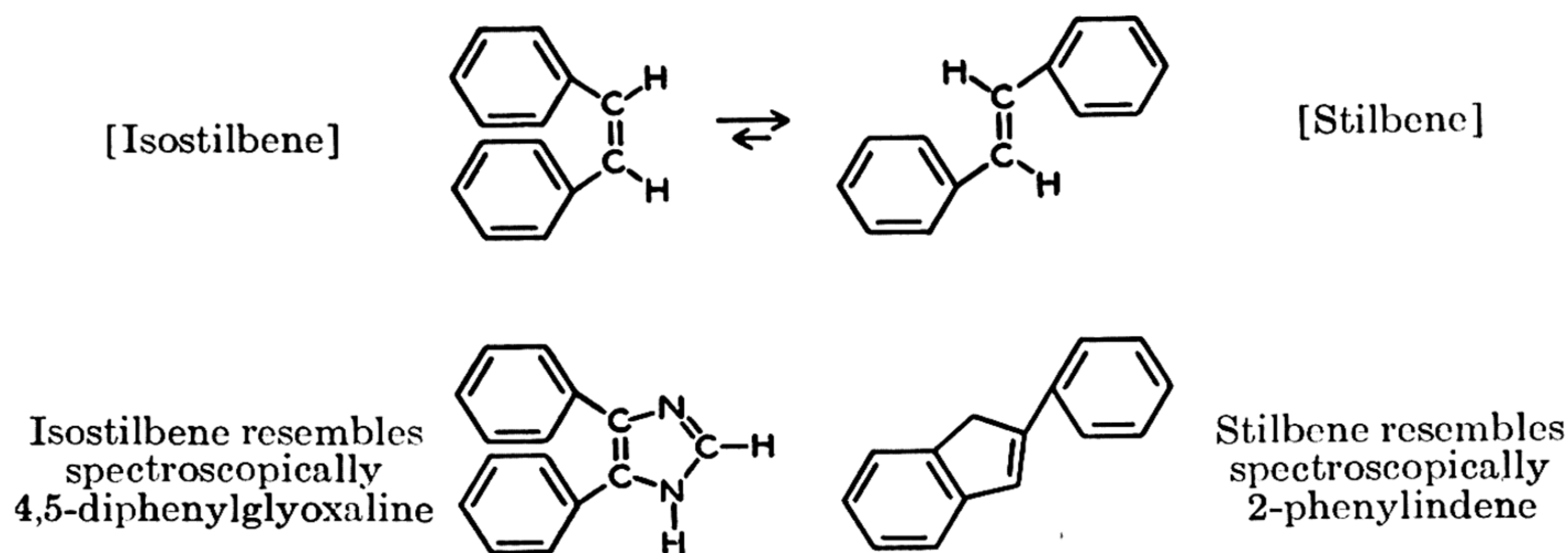
p-Diallylbenzene formed a mixture of *p*-allylpropenylbenzene and *p*-dipropenylbenzene when slowly conducted over alumina at 300° in the presence of carbon dioxide.^{342a} These isomerizations probably proceed in two steps:



1,1-Diphenylethylene, when passed 2 or 3 times over infusorial-earth briquettes at 500°, was converted into *trans*-1,2-diphenylethylene (*i.e.*, stilbene):⁴⁵⁶



In the case of isomerizations in the 1,2-diphenylethylenes, there occurs a typical *cis-trans* conversion.^{306, 567} It is a noteworthy fact that the ultraviolet absorption spectrum of *cis*-1,2-diphenylethylene (*i.e.*, isostilbene) resembles that of 4,5-diphenylglyoxaline, whereas that of the *trans*-form resembles 2-phenylindene:⁶⁴⁵

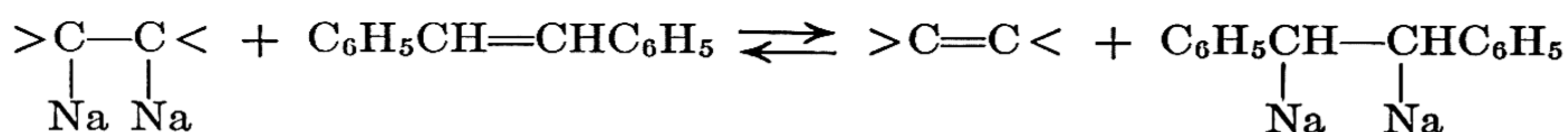


The thermal isomerizations of vaporized *cis*-1,2-diphenylethylene (*i.e.*, isostilbene) and of the *trans* form (stilbene) at 320-341° were found to be reversible and unimolecular.³⁰⁶ The activation energy amounted to 43 kilocalories per gram-mole. The equilibrium composition (starting with pure stilbene) is 7 per cent *cis* and 93 per cent *trans* form. These values may be erroneous, since the corresponding calibration curve³⁰⁶ for the fusion of stilbene-isostilbene mixtures had an impossible curvature.⁵⁷⁸

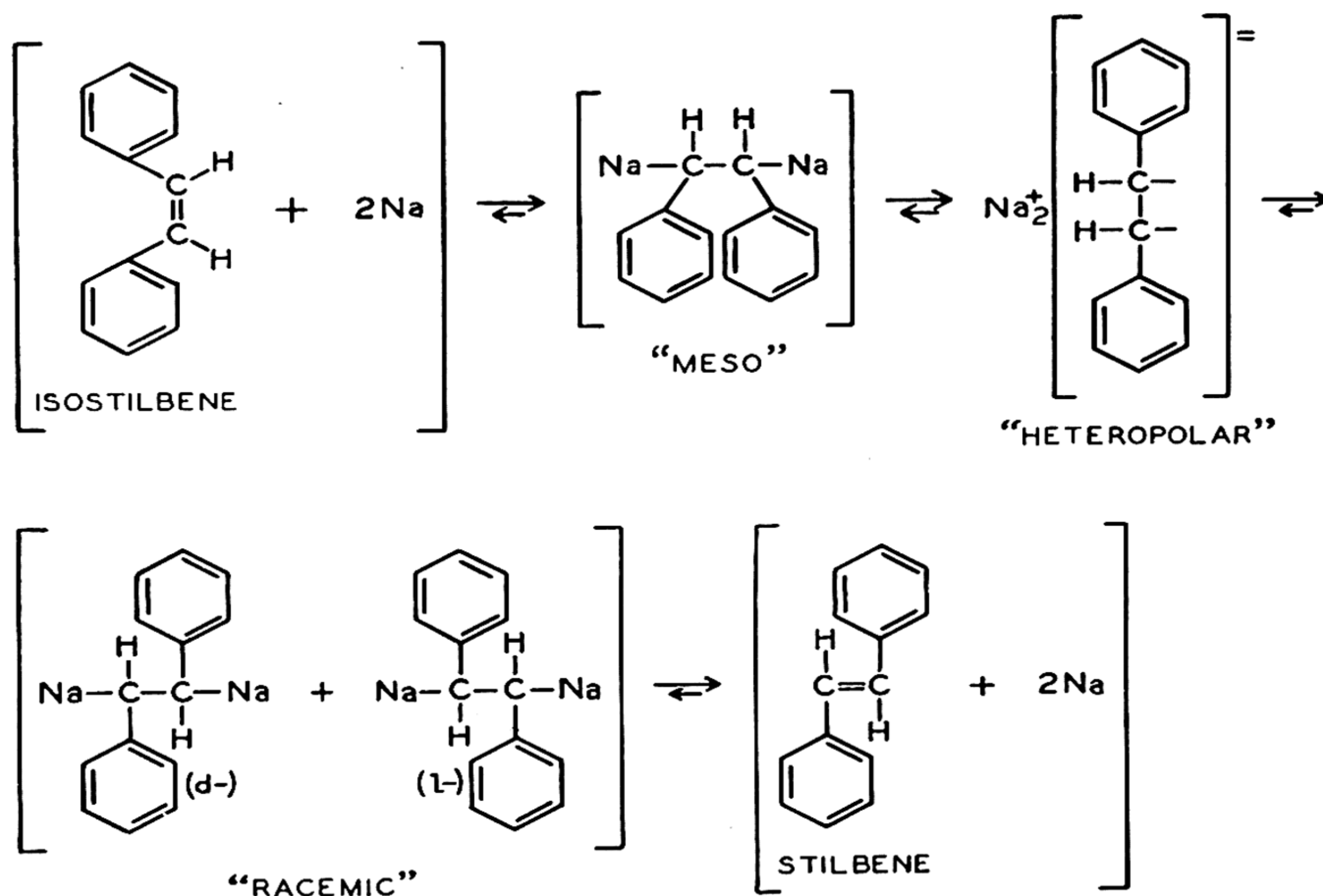
Exposure of hexane solutions of stilbene to ultraviolet light (3130Å) resulted in the formation of isostilbene with "100 per cent" quantum efficiency.⁵⁵⁶ Similarly, isostilbene was obtained after the exposure of a benzene solution to ultraviolet light for 8 days.⁵⁶⁷ Recent work^{350a} indicates that the exposure of an "iso-octane" solution of stilbene to ultraviolet light (2537Å) is attended by an isomerization of 35 per cent of the excited molecules to isostilbene. The remaining, excited stilbene molecules return to their original state by undergoing fluorescence (48 per cent) or by exchanging their excess electronic energy for rotational and vibrational energies (17 per cent).

Isostilbene has been converted into stilbene by heat, sunlight, ultraviolet light, certain elements, boron fluoride,⁴⁴⁷ and various acids. The *thermal* conversion of isostilbene into stilbene has been investigated at temperatures around 170°,^{567, 572} 277°,⁶⁵² and 320°.³⁰⁶ The isomerization of isostilbene by sunlight^{428a, 572, 652} is accelerated remarkably by a trace of iodine.^{572, 652} Exposure to sunlight of a carbon disulfide solution of isostilbene containing a trace of bromine gave stilbene.⁵⁶⁷ Irradiation of an "iso-octane" solution of isostilbene by ultraviolet light (2537Å) was followed by the formation of 29 per cent of stilbene, and the reformation of 68 per cent of isostilbene, from the electronically excited molecules.^{350a} Treatments of ethereal isostilbene solutions with lithium or sodium gave colored addition compounds, which were decomposed subsequently by carbon dioxide and alcohol, respectively.⁵¹⁶ These metalations-demetalations gave stilbene, but the yields were not reported.

Traces of stilbene-disodium or of stilbene-dilithium, in the complete absence of free alkali-metals, changed isostilbene instantly into stilbene with strong evolution of heat.⁶⁸⁰ The discovery of the last reaction led to the theory that the organoalkali compounds dissociate readily in the following manner:⁶⁸⁰



The stilbene-dialkali compounds, moreover, were stated to have probably 3 tautomeric forms: a spatially undefined pure-heteropolar tautomer, a racemic (*dl*) form, and a meso form. The heteropolar tautomer is a form common to the racemic and meso forms. The last two forms, upon demetalation, would lead to stilbene and isostilbene, respectively; hence the catalysis by the dialkali compounds can be formulated as the following right shift of reactions, which illustrates the postulated sodium-ion transfers.



Random addition of one sodium atom at a time to the ethylene linkage has been advanced to explain carboxylation and methylation of 1,2-diphenylethylene.⁶⁵⁵

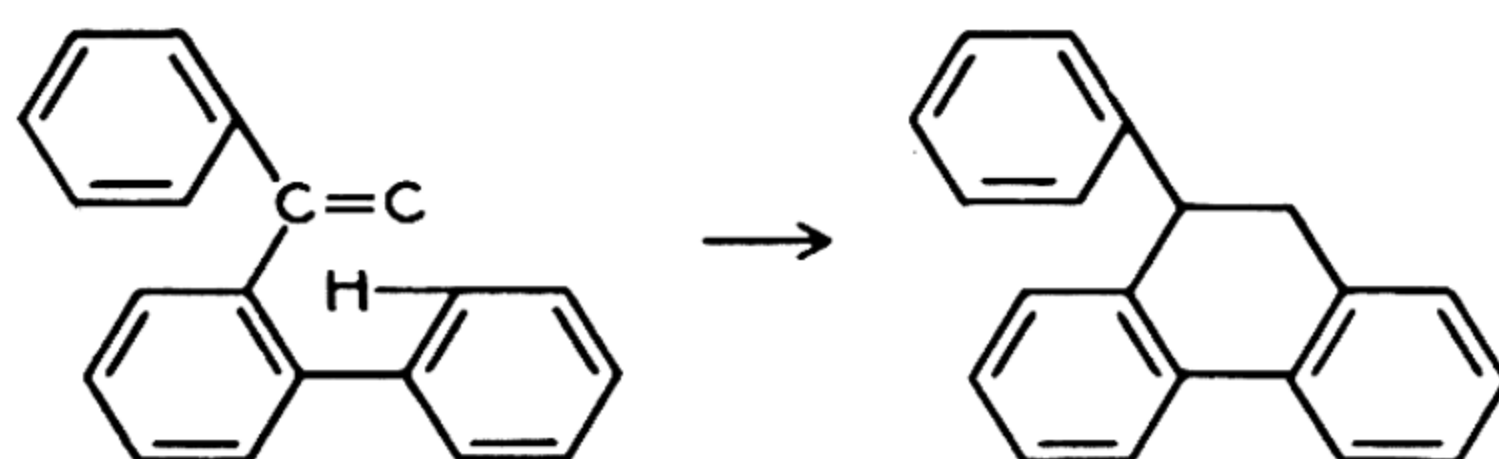
Isostilbene was converted into stilbene by treatment with hydrogen bromide when aided by any of the following agents: heat,⁶⁰⁸ artificial light,³⁰³ sunlight,³⁰³ reduced copper or iron,⁶⁰⁸ reduced nickel,^{607, 608} palladium or platinum blacks,⁶⁰⁸ air,⁶⁰⁸ oxygen,⁶⁰⁷ ascaridole,³⁰³ or benzoyl peroxide.^{303, 607} Some work indicates that hydrogen bromide plus air does not readily isomerize isostilbene in benzene solution in the dark.³⁰³

Catechol, hydroquinone, ethyl mercaptan, and thiophenol are effective inhibitors in the isomerization of isostilbene by hydrogen halides.³⁰³ Isostilbene "boiled" with 20-per cent hydrochloric acid gave stilbene;⁵⁷⁰ hydrogen chloride was ineffective at room temperature in the presence of either ascaridole or benzoyl peroxide.³⁰³ Exposure of isostilbene to vapors of fuming nitric acid gave stilbene;^{300, 567, 572} this method is reminiscent of the isomerization of oleic into elaidic acid. From these experiments, it follows that several interpretations may be given to the reactivity of alkenes and their catalysts. For instance, it is claimed that isomerization induced by hydrogen bromide is due to oxidation into bromine,³⁰³ to an excitation of hydrogen bromide,^{607, 609} or to the paramagnetic behavior of bromine atoms which enables them to interact with the double bond.³²⁴ In several cases, however, purely thermal isomerization appears to be an adequate explanation.

Recently, benzoic acid was used as a catalyst for the liquid-phase reactions between isostilbene and stilbene at 200° in an atmosphere of nitrogen.⁵⁷⁸ Starting from either isomer, the same equilibrium mixture, 4 per cent isostilbene and 96 per cent stilbene, was obtained. The heat of activation of isostilbene at 214-223° was found to be 36.7 kilocalories per gram-mole. An oxygen atmosphere, used in place of nitrogen and benzoic acid, led to the formation of an organic-acid product that converted isostilbene into stilbene.⁵⁷⁸ Addition of hydrogen chloride to a nitrogen atmosphere was sufficient "to convert isostilbene into stilbene in 4 hours at 190°." ⁵⁷⁸

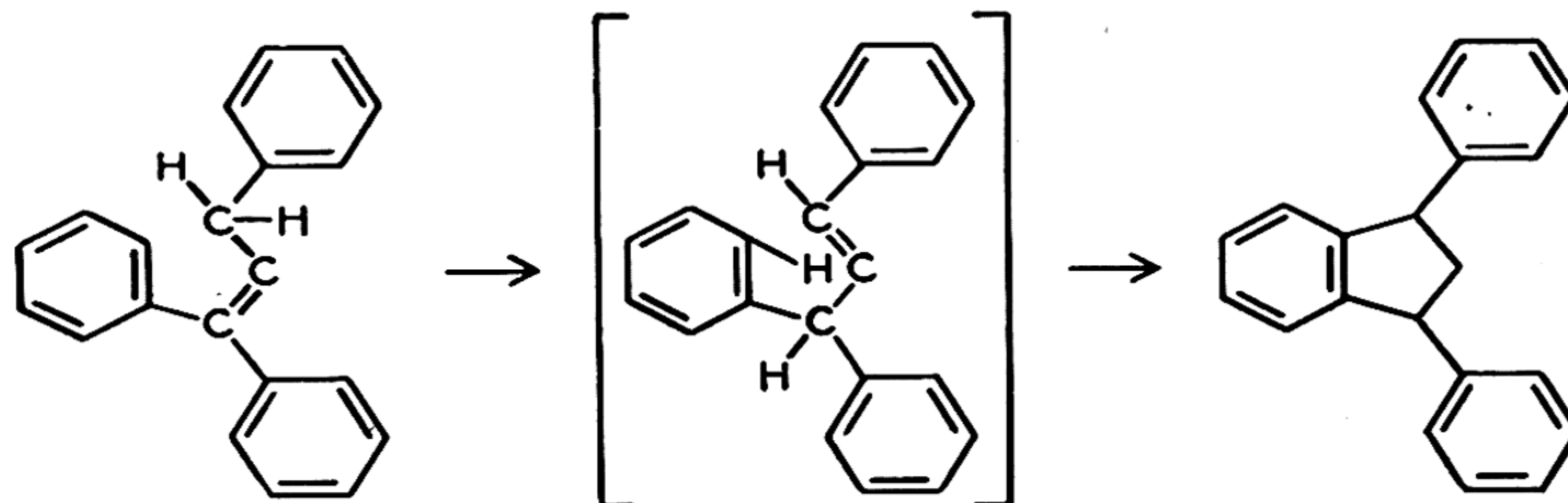
It is the opinion of the authors that the mechanism of isostilbene-stilbene isomerization parallels that of *cis*- and *trans*-butene-2. These transformations, therefore, should be investigated by means of parallel studies. It may be pointed out that the conditions (heat and/or presence of boron fluoride, oxidizing agents, or acids) reported as favorable for the conversion of isostilbene into stilbene are those of energy addition or the presence of catalysts having electron-deficient natures. These two factors enable the double bond to be opened temporarily by movement of electrons.

o-Phenyl-1,1-diphenylethylene was cyclized by phosphorus pentachloride into 9-phenyl-9,10-dihydrophenanthrene:⁵⁰

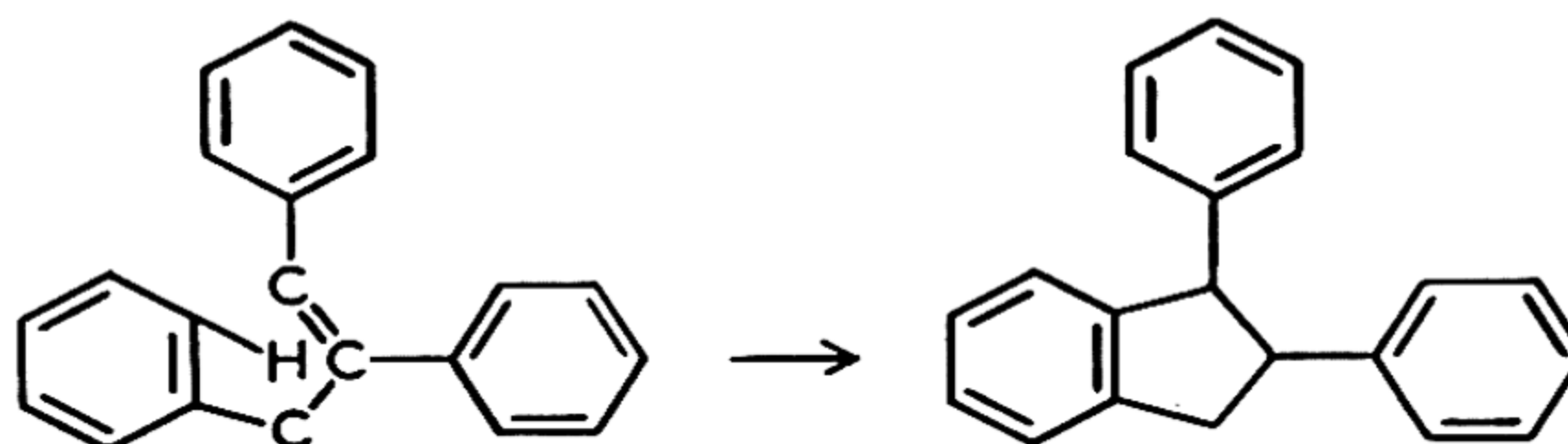


1,1,3-Triphenylpropene-1, when treated for 8 days with concentrated sulfuric acid, gave 16 per cent of 1,3-diphenylindane.⁵¹⁷ A 10 per cent

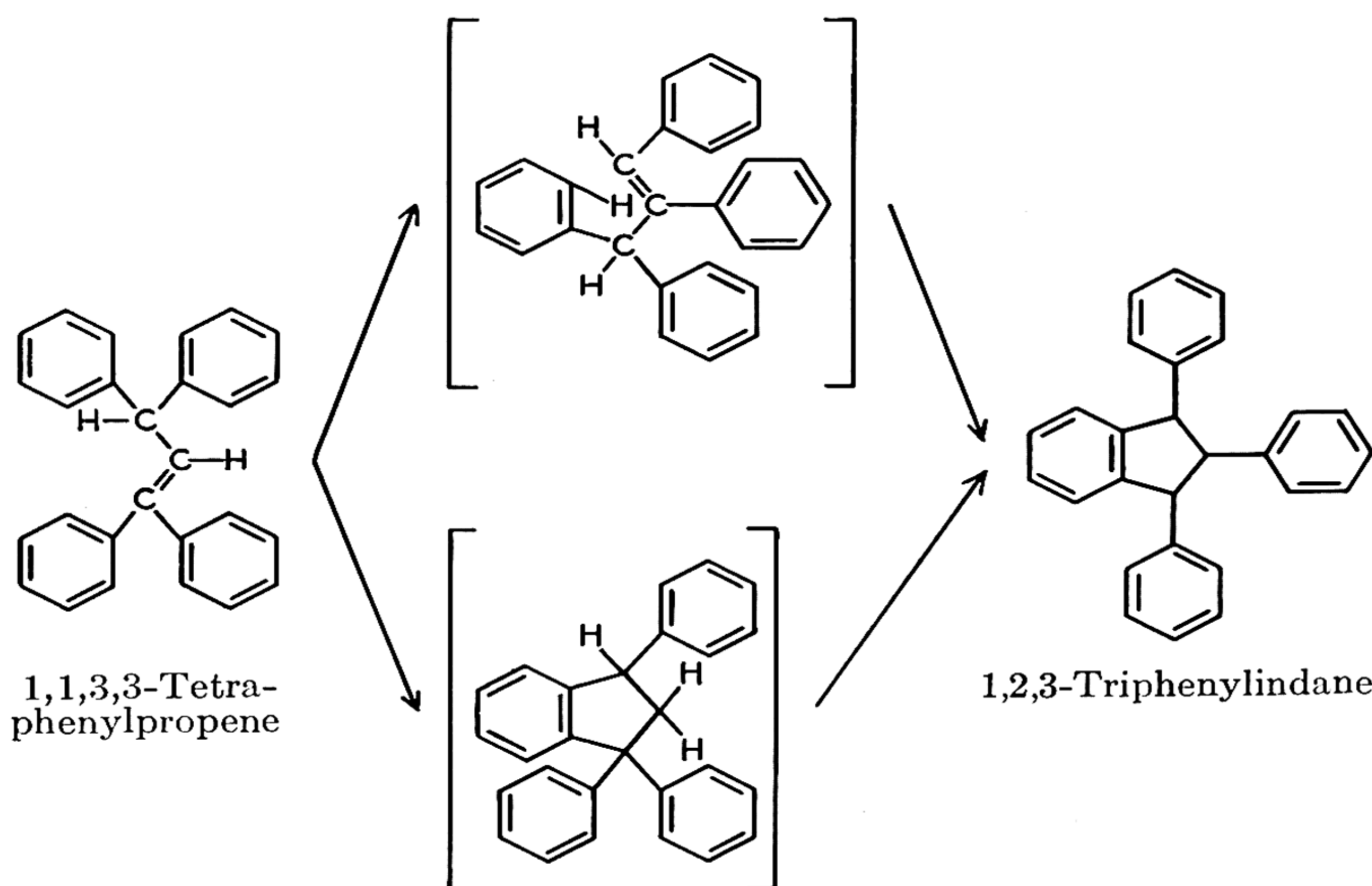
yield of 1,3-diphenylindane resulted when diphenylbromomethane acted in ether upon the organolithium compound of 1,1,3-triphenylpropene-1.⁵¹⁸ These isomerizations can be explained as a transient conversion into 1,3,3-triphenylpropene-1 (*i.e.*, 1,1,3-triphenylpropene-2), followed by cyclization:⁵¹⁷



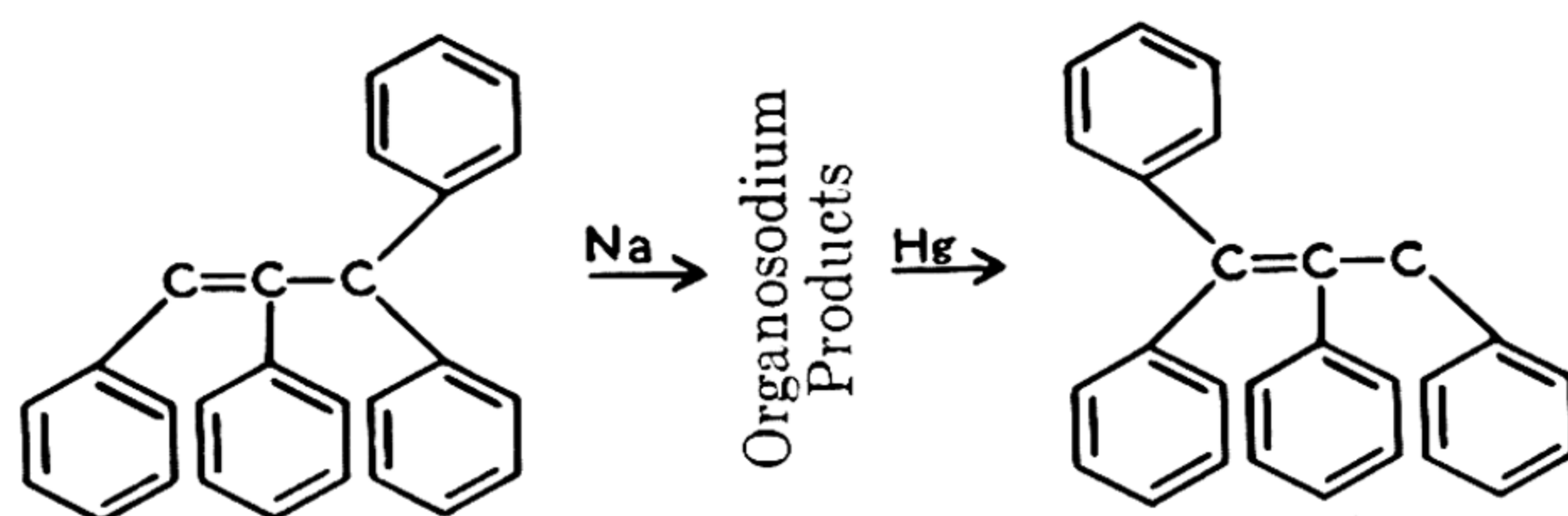
1,2,3-Triphenylpropene probably can be isomerized to 1,2-diphenylindane:⁵²



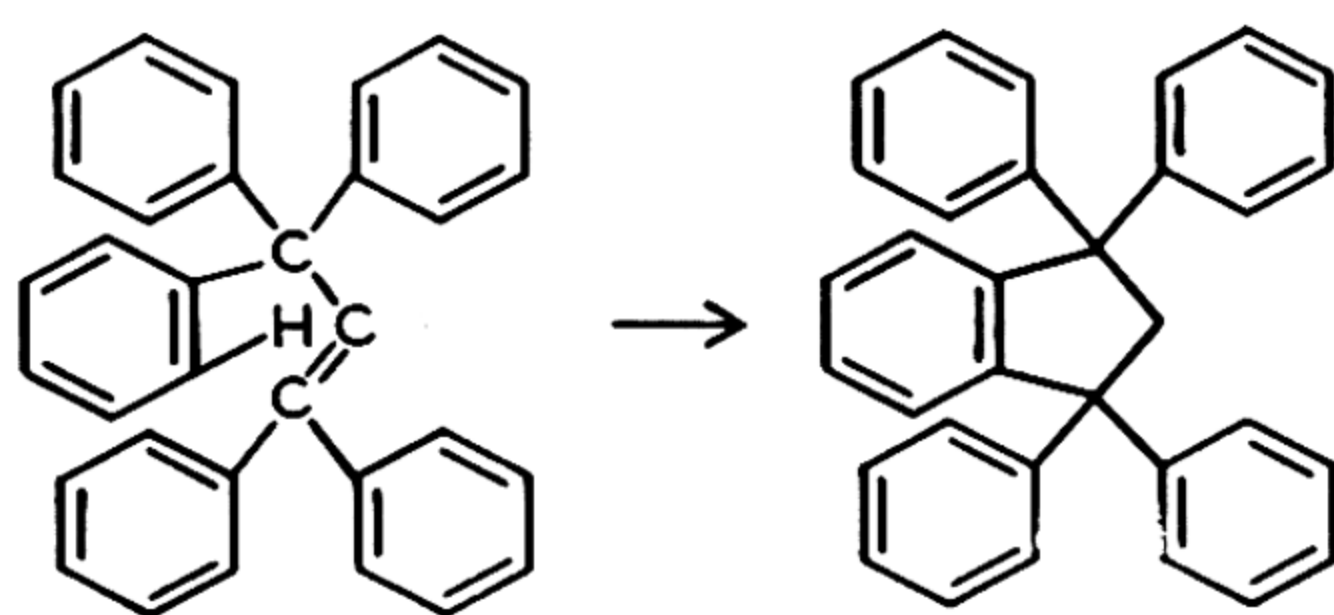
1,1,3,3-Tetraphenylpropene, when dissolved in ether and shaken for 8 days with lithium, formed a soluble lithium derivative which was hydrolyzed later by alcohol into 1,2,3-triphenylindane.⁵¹⁶ The reaction has not been explained. The following equations are proposed by the authors:



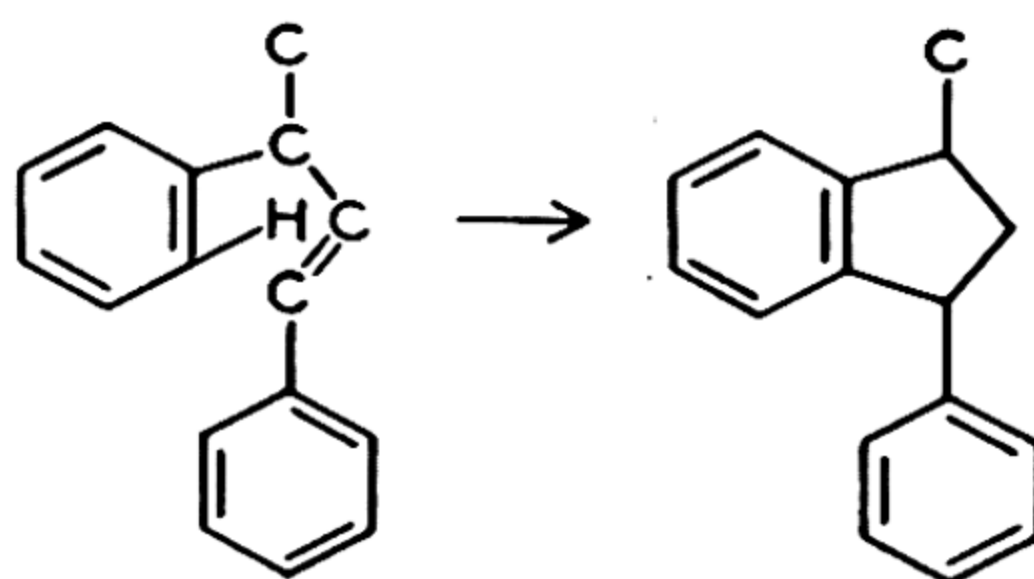
1,2,3,3-Tetraphenylpropene-1 (*i.e.*, 1,2-diphenyl-1-benzhydrylethylene, m.p. 131°) was isomerized to 1,1,2,3-tetraphenylpropene-1 (*i.e.*, 1,1,2-triphenyl-2-benzylethylene, m.p. 142°) by conversion into organosodium products by means of sodium metal, followed by a demetalation in the presence of mercury.⁵³ A considerable amount of 1,1,2,3,4,5,6,6-octaphenylhexadiene-1,5 occurs in this reaction as a by-product, due to a Würtz-type condensation.



1,1,3,3,3-Pentaphenylpropene was isomerized to 1,1,3,3-tetraphenylindane when boiled with a 4 per cent solution of sulfuric acid in acetic acid:³¹⁶



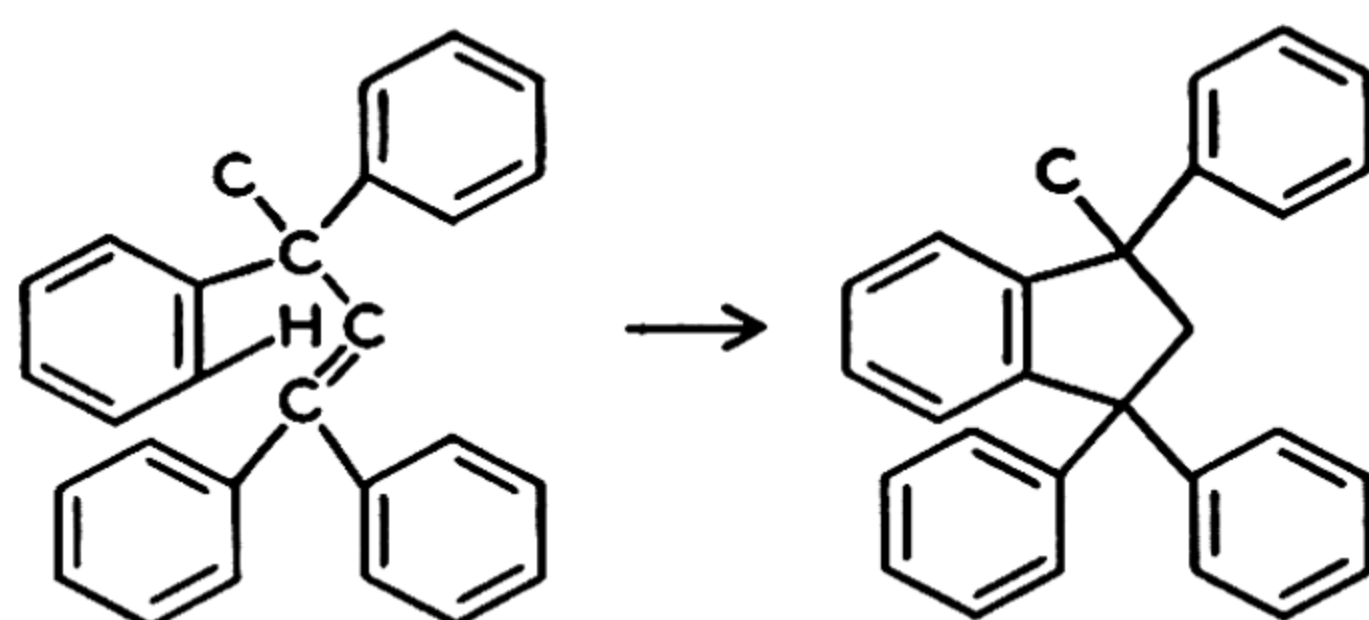
1,3-Diphenylbutene-1, which is termed "liquid distyrene" in the literature, is believed to undergo a very slow isomerization in the presence of traces of sulfuric acid.⁵⁶⁹ The product was reported to be 1,3-diphenylbutene-2,⁵⁶⁹ but it is probably 1-methyl-3-phenylindane.⁴⁶⁸ The last hydrocarbon was produced by heating 1,3-diphenylbutene-1 for 40 hours under reflux with dilute sulfuric acid:⁴⁶⁸



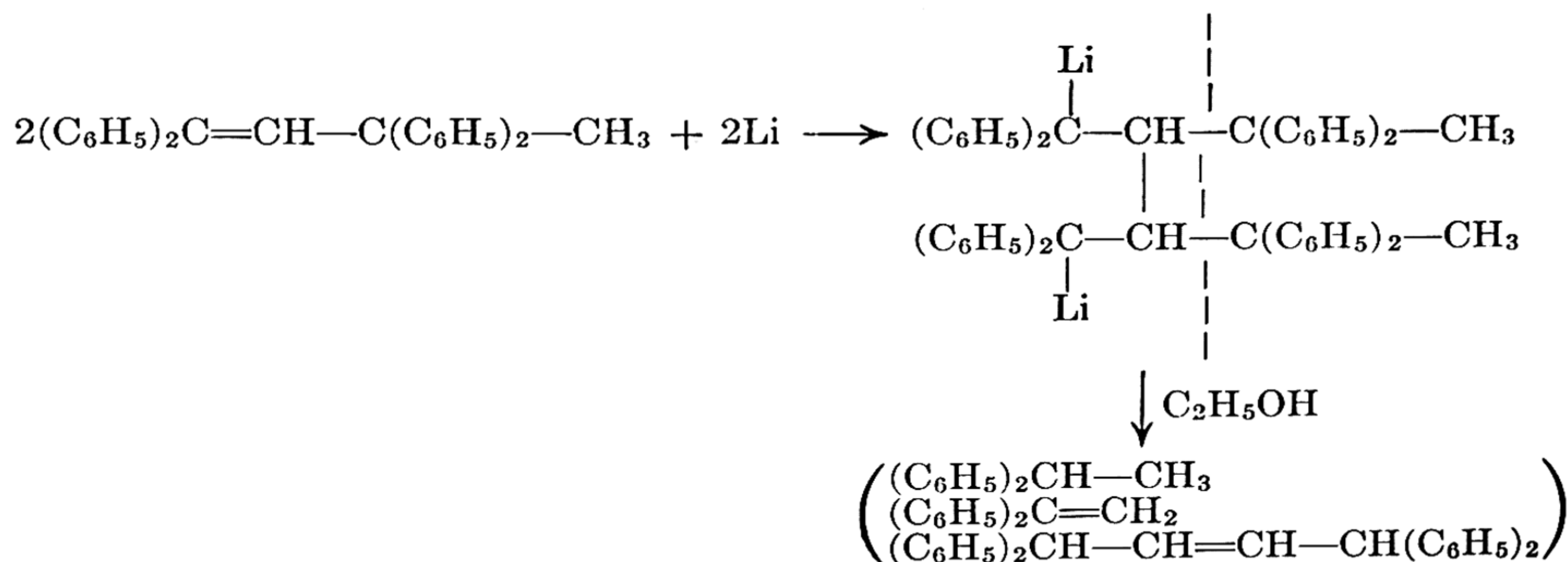
2,3-Diphenylbutene-2 occurs in a "stable" α -form (m.p. $65-66^{\circ}$) and an "unstable" β -form (m.p. 104°). These are stated to be an exception to the general rule: "the most stable geometrical isomer has the higher

melting point.”⁴⁵⁸ The β -form, when heated for a few minutes with sulfuric acid-treated pumice, and then distilled *in vacuo*, gave irreversibly over 5 per cent of the α -form.⁴⁵⁸

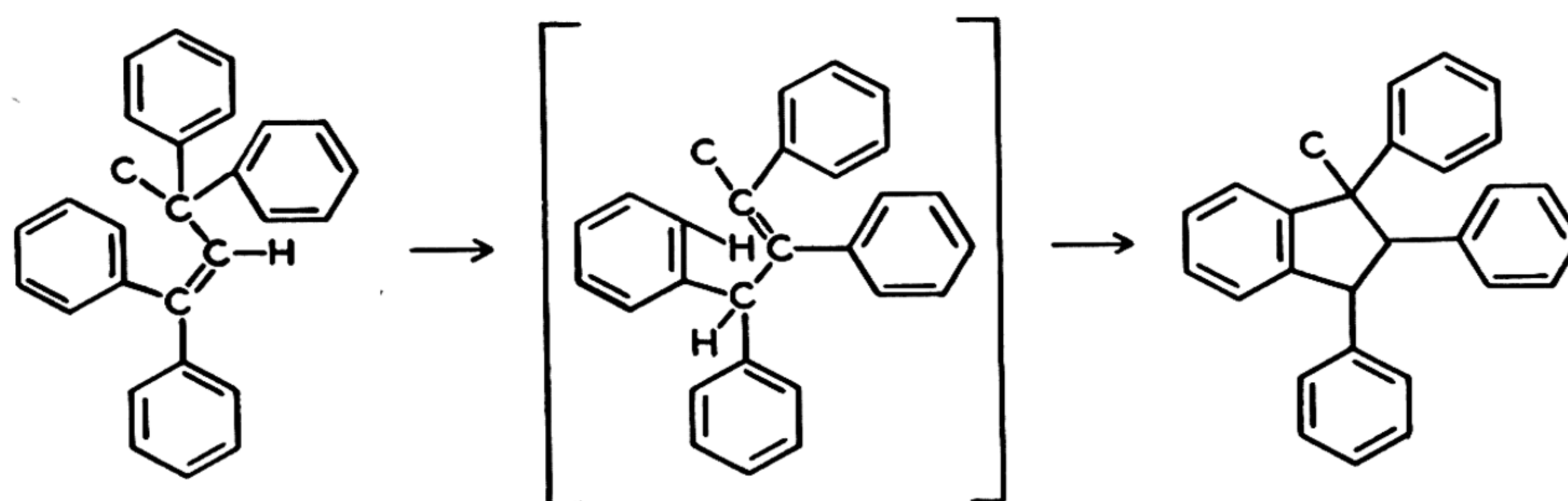
1,1,3,3-Tetraphenylbutene cyclized at 215° in the presence of “Floridin” into 1-methyl-1,3,3-triphenylindane.³³² The product³³² was taken erroneously to be 1,1,3,3-tetraphenylcyclobutane.^{54, 522} 1,1,3,3-Tetraphenylbutene was converted also into the indane by treatment with concentrated sulfuric acid,⁵⁴ stannic chloride plus benzene partly saturated with dry hydrogen chloride,⁵²² dimethylsulfate,^{43a} and probably by iodine in a slow cyclization at 100°.⁵⁴ The isomerization is obviously an “internal alkylation” of a 3-phenyl group at its ortho position:



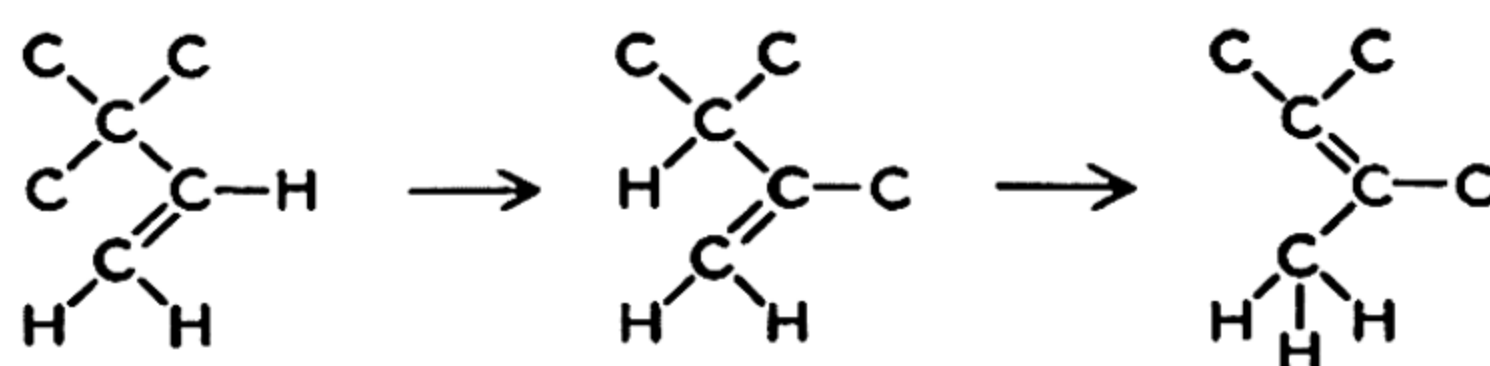
The isomerizations of 1,1,3,3-tetraphenylbutene into 1,1,4,4-tetraphenylbutene-2 and 1-methyl-1,2,3-triphenylindane, which result when the organolithium compound of the first hydrocarbon is hydrolyzed by alcohol, were explained as follows:⁵⁵



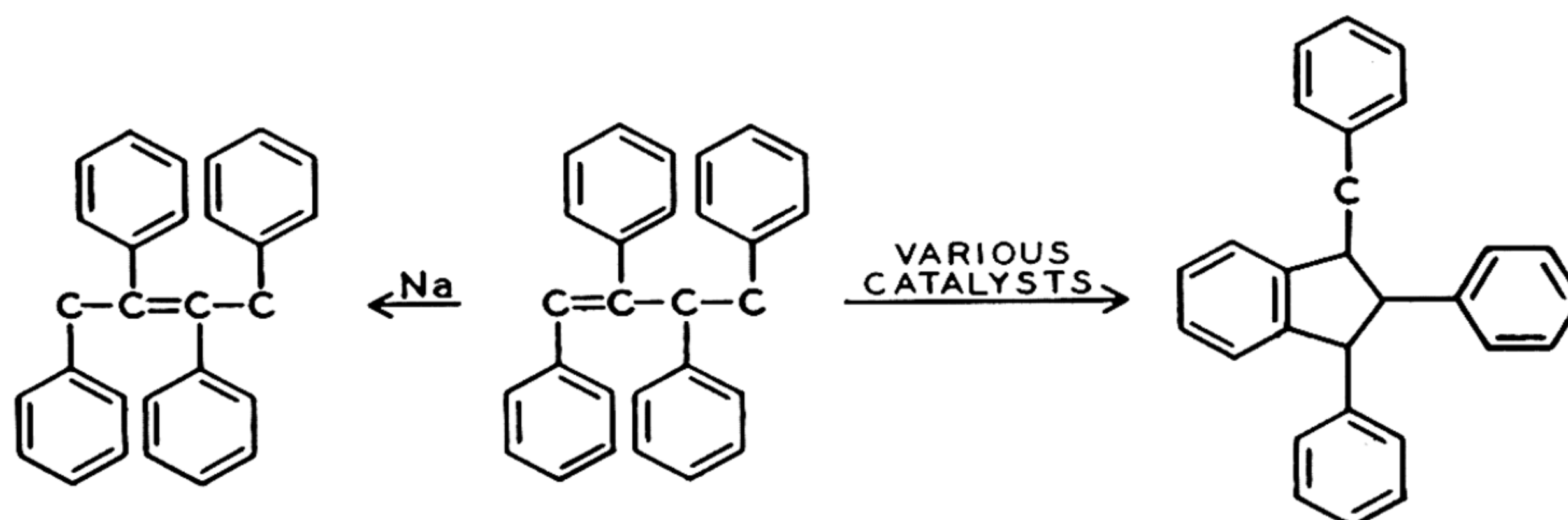
The formation of 1-methyl-1,2,3-triphenylindane was stated (without further explanation) to result from the migration of a phenyl group. This product requires the isomerization of 1-methyl-1,3,3-triphenylindane (the expected product), or that of 1,1,3,3-tetraphenylbutene into 1,2,3,3-tetraphenylbutene or 1,1,2,3-tetraphenylbutene-2. The interpretation of the reaction as the conversion of 1-methyl-1,3,3-triphenylindane finds support in the known isomerizations of aryl indenenes, whereas the postulated cyclization of 1,1,2,3-tetraphenylbutene-2:



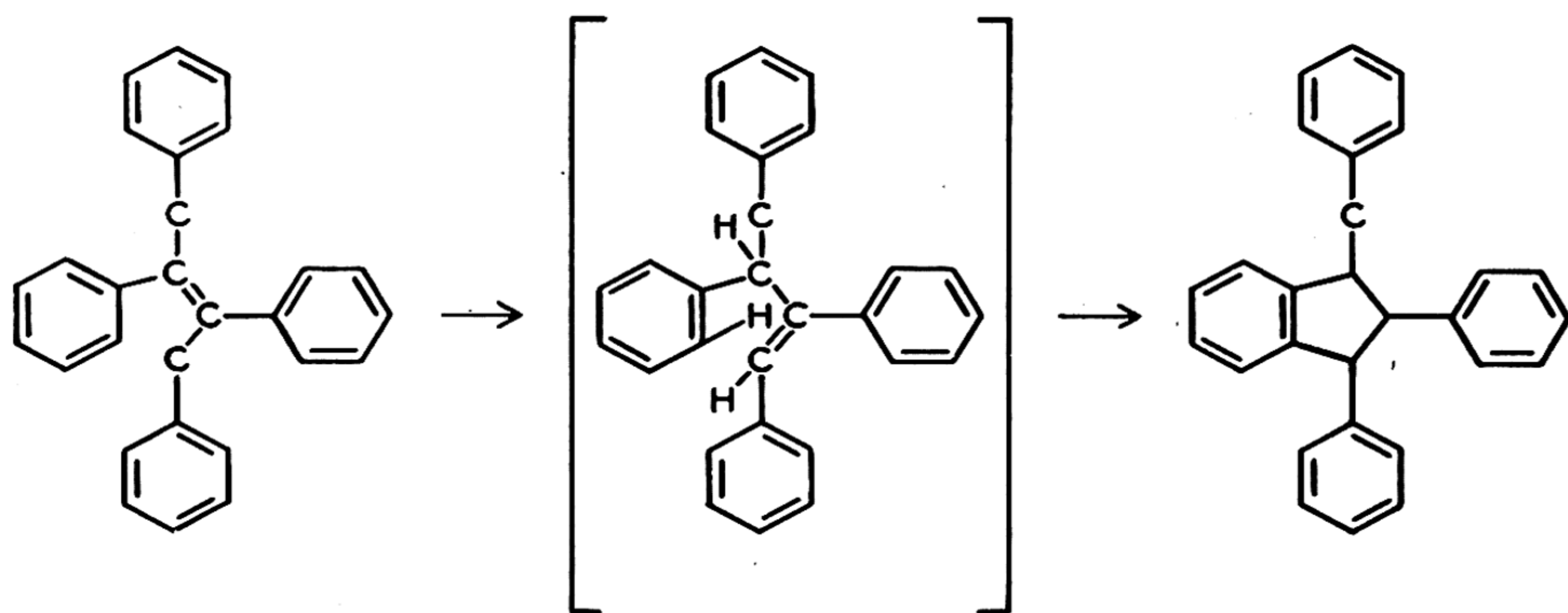
corresponds to the "right-shift" of reactions shown by 3,3-dimethylbutene:



1,2,3,4-Tetraphenylbutene-1 occurs in a geometrical form of m.p. 96° and a more reactive form of m.p. 150° .⁵⁷ The treatment of the less reactive form (in ether) with sodium, and then with alcohol, led to the formation of 1,2,3,4-tetraphenylbutene-2 with m.p. 80° . The other form, when treated in the same manner, cyclized into 1-benzyl-2,3-diphenylindane and isomerized only slightly into 1,2,3,4-tetraphenylbutene-2. The same cyclization ensued in experiments on the more reactive form using: (a) sodium in boiling amyl alcohol, (b) stannic chloride plus hydrogen chloride-saturated benzene, or (c) red phosphorus, concentrated hydriodic acid, plus acetic acid under reflux:

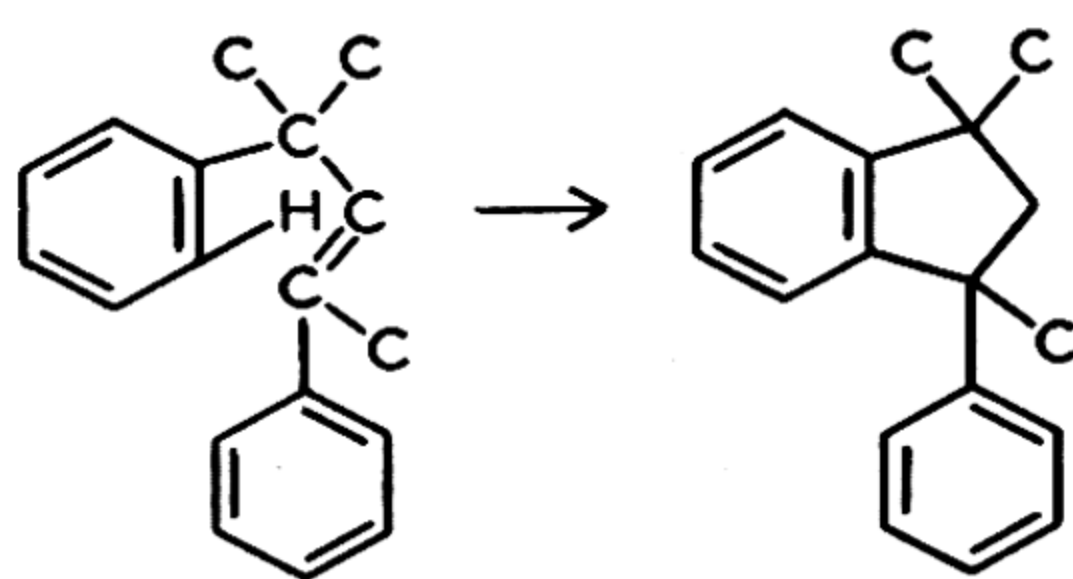


1,2,3,4-Tetraphenylbutene-2 (melting point 80°) was converted into 1-benzyl-2,3-diphenylindane upon high-vacuum distillation or by treatment in ether with sodium followed by alcohol.⁵⁷ The investigators assumed that a preliminary conversion into 1,2,3,4-tetraphenylbutene-1 occurs in the treatment with sodium:



This proposal, and the *cis-trans* orientations of aryl groups about the double bond of these butenes, remain to be investigated.

2,4-Diphenyl-4-methylpentene-2, when treated with aluminum chloride plus benzene for 2 days, or with stannic chloride for 20 hours, gave respectively 20 and 40 per cent of 1,1,3-trimethyl-3-phenylindane: ⁵¹



Isomerizations of the alkenyl benzenes are given in Table 36, p. 366.

Conclusions

1. Isomerizations of alkenyl benzenes by shift of the double bond within the unsaturated side-chain occur under the influence of heat; these isomerizations are aided by catalysts, such as alcoholic potash, alumina, chromia, palladium, platinum, nickel-on-asbestos, and infusorial earth.

2. The resulting isomers are formed by a stepwise migration of the side-chain double bond toward the ring (eventually, conjugation with the ring double bonds).

3. Cyclizations of alkenyl benzenes occur under the influence of strong acids, such as phosphoric and sulfuric acids, and miscellaneous catalysts ("Floridin," iodine (?), lithium, sodium, aluminum chloride, stannic chloride, and phosphorus pentachloride).

4. The catalytic activity of "Floridin," iodine, aluminum chloride, stannic chloride, and phosphorus pentachloride may be attributed to the presence of acids. These acids are those (a) used in the initial activation of the "Floridin," (b) produced by the action of iodine on hydrocarbons (liberating hydrogen iodide), and (c) formed by hydrogenation-

hydrolysis (*e.g.*, hydrogenolysis) of the aluminum chloride, stannic chloride, or phosphorus pentachloride (liberating hydrogen chloride). The activity of lithium and sodium may be due to the formation of "lithium hydride" and "sodium hydride," respectively, since an isomerization with phenyl migration involves obviously a momentary loss of labile hydrogens.

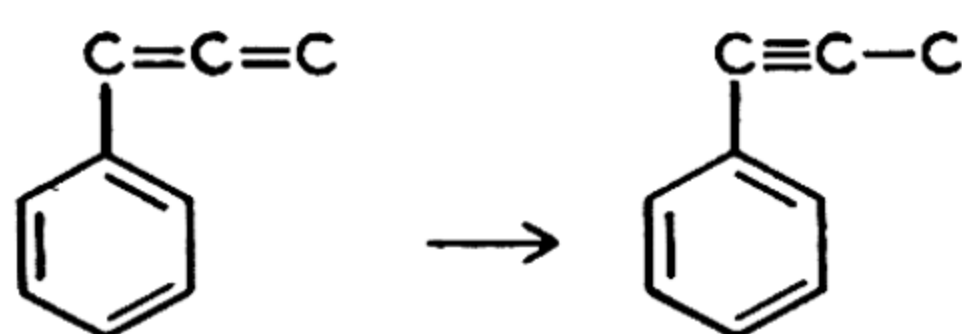
5. The typical *cis-trans* isomerization in the case of 1,2-diphenylethylene (stilbene and isostilbene) has been studied extensively. Thermally, it probably proceeds in a manner analogous to that of butene-2, by a transfer of hydrogen with the "opening and closing" of the double bond (via partial break and rotation, or by the formation of a new tetrahedron). Such a mechanism seems preferable to an interchange of a hydrogen atom and a phenyl group. In the case of the corresponding catalytic interconversions, it seems necessary to postulate the *cis-meso-heteropolar-racemic-trans* shifts.

ALKADIENYL BENZENES

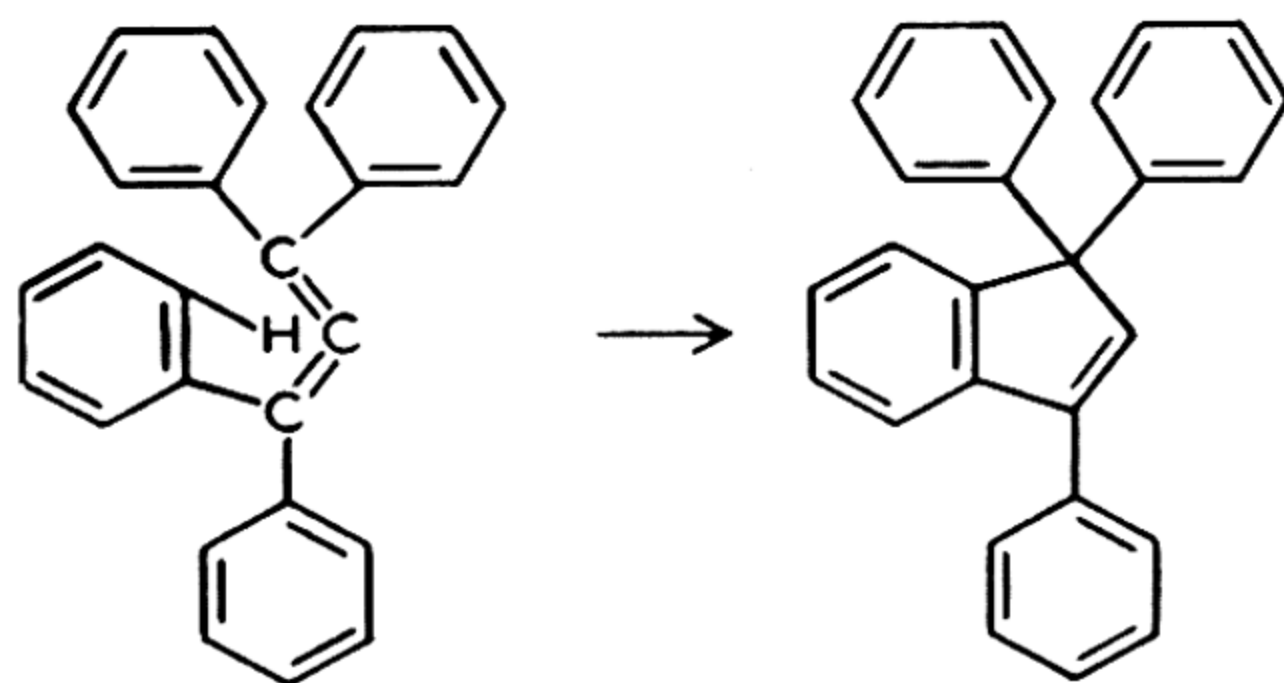
The alkadienyl benzenes are either allenic or non-allenic in structure. Side-chains in these hydrocarbons do not undergo an extensive interconversion of double bonds, in contrast to the behavior of the aliphatic alkadienes.

Allenic Alkadienyl Benzenes

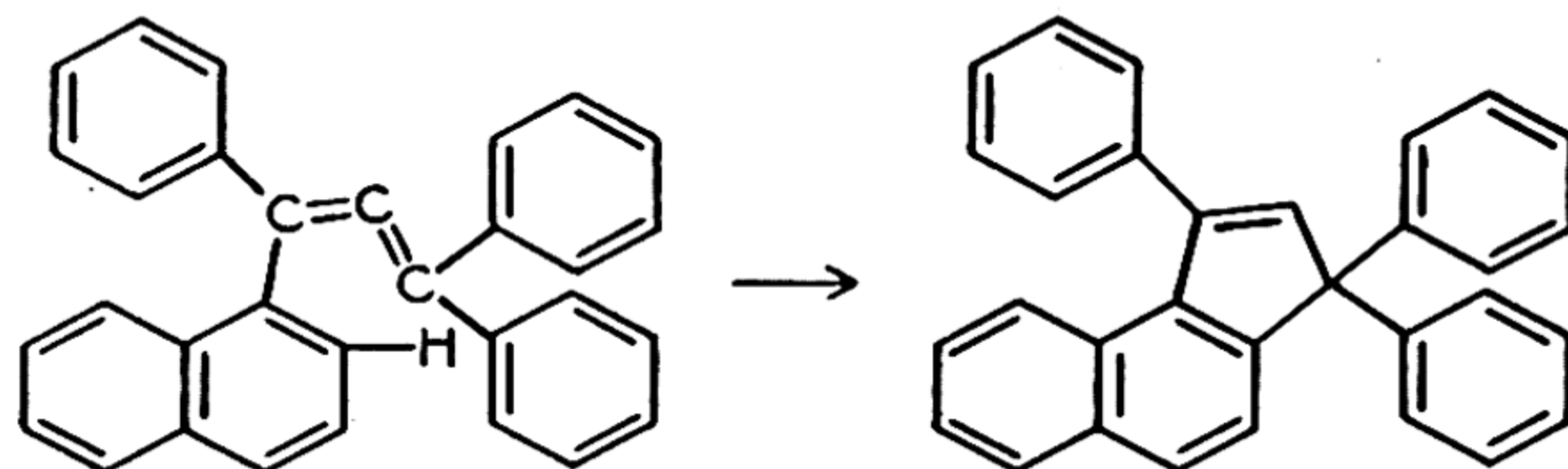
Phenylpropadiene (*i.e.*, phenylallene) isomerized to 1-phenylpropyne-1 under the action of alcoholic potash at 105-110° for 6.5 hours: ²¹⁴



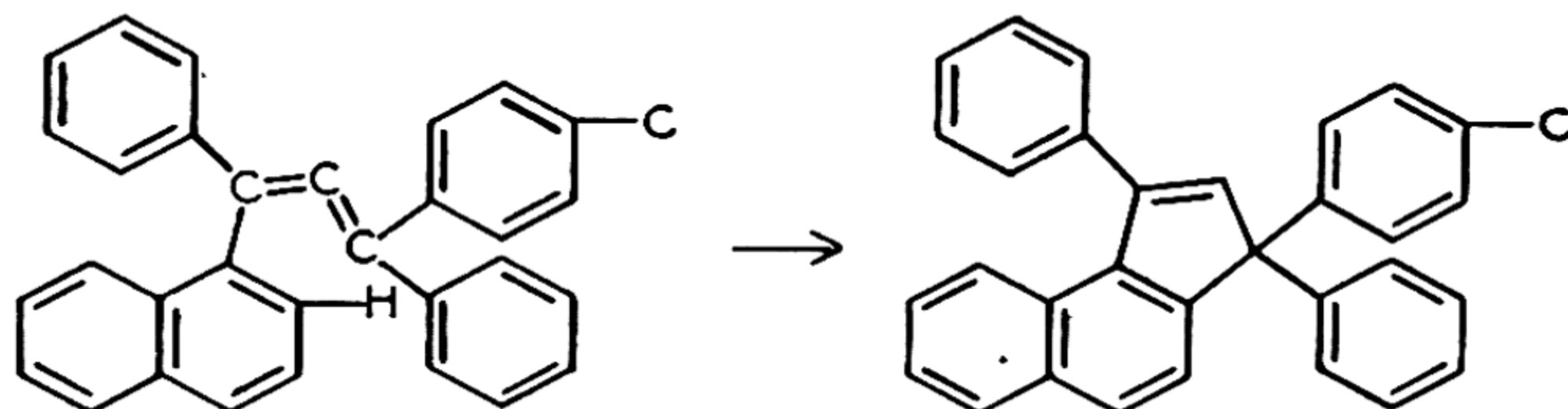
Tetraphenylpropadiene (*i.e.*, tetraphenylallene) was cyclized to 1,1,3-triphenylindene by treatment with: (a) iodine in benzene, (b) hydrogen bromide and hydrogen chloride as gases, or their saturated solutions in acetic acid, (c) boiling "concentrated" hydrochloric acid, or (d) boiling acetic acid.⁶¹³ Acetic acid, saturated with hydrogen chloride at the boiling point, is an effective catalyst.³¹⁷



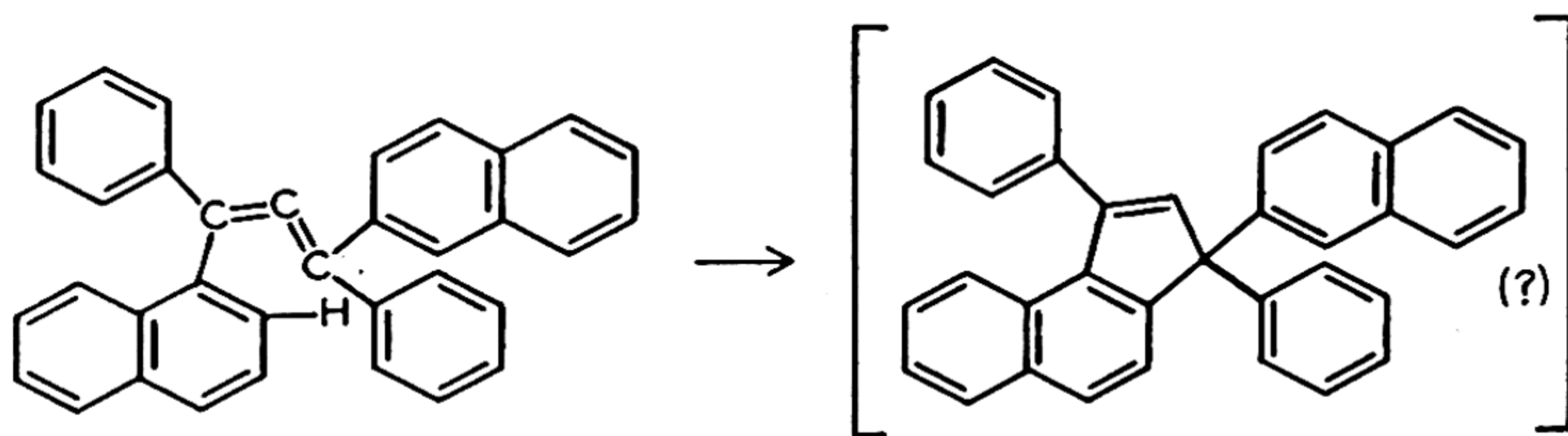
Triphenyl-(1-naphthyl)-propadiene, when heated under reflux with hydrogen chloride in acetic acid, or with *p*-toluenesulfonic acid in benzene, formed 1,3,3-triphenyl-3- α -naphthindene (*i.e.*, 1,1,3-triphenyl-4:5-benzindene): ¹⁰⁶



1,3-Diphenyl-1-*p*-tolyl-3-(1-naphthyl) propadiene, treated with hydrogen chloride in acetic acid, was isomerized to 1,3-diphenyl-3-*p*-tolyl-3- α -naphthindene (*i.e.*, 1,3-diphenyl-1-*p*-tolyl-4:5-benzindene): ¹⁰⁶

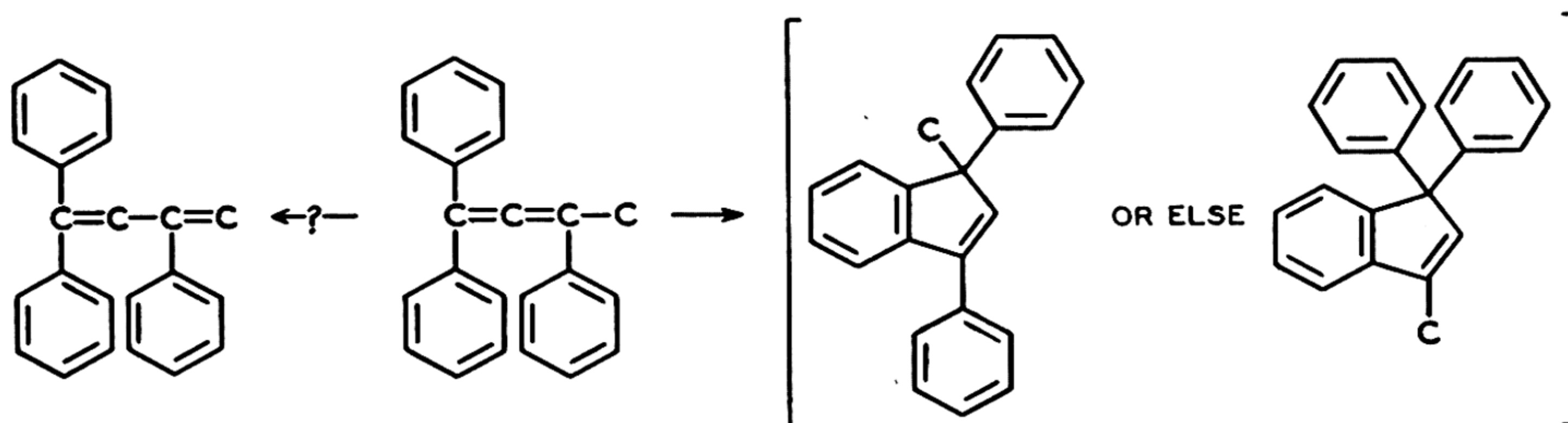


d-1,3-Diphenyl-1,3-di-(1-naphthyl) propadiene was racemized at the boiling point of decalin used as solvent.³⁵⁸ The racemate, heated for 5 minutes with hydrogen chloride plus acetic acid, or for one hour with iodine in benzene, was cyclized to an isomer (m.p. 233-234°) taken to be 1,3-diphenyl-3-(1-naphthyl)-3- α -naphthindene (*i.e.*, 1,3-diphenyl-1- α -naphthyl-4:5-benzindene.³⁵⁸ This assigned structure is tentative, since the formations of 1-phenyl-1,3-di-(1-naphthyl)indene and 1,3-diphenyl-1-(1-naphthyl) benzonaphthene (*i.e.*, 1,3-diphenyl-1-(1-naphthyl)-perinaphthindene) were not excluded definitely:



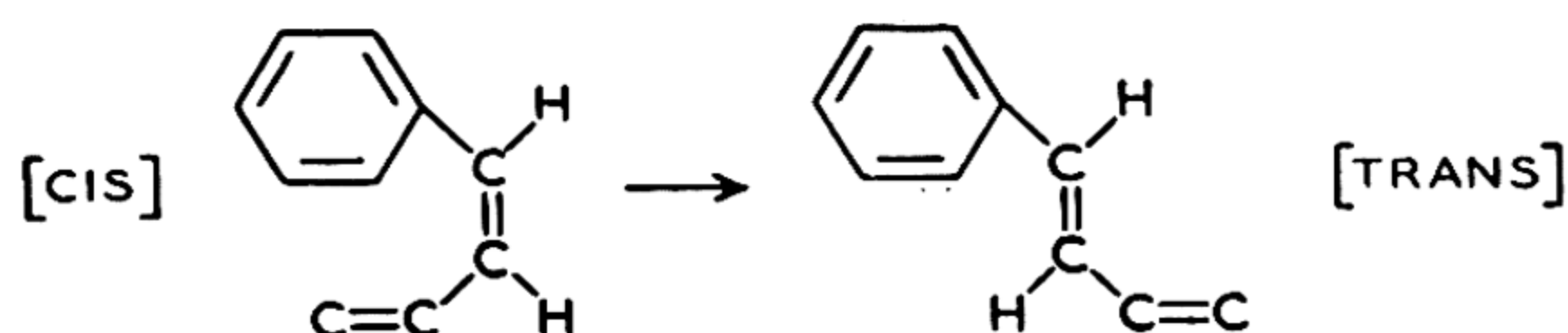
1,1,3-Triphenylbutadiene-1,2, treated with acetic acid plus sulfuric acid, gave a liquid product slowly crystallizing, in part, to a methyl-diphenylindene (m.p. 56°).⁶⁷⁹ Theoretically, this cyclization product can be expected to contain 1-methyl-1,3-diphenylindene and 1,1-diphenyl-3-methylindene. Boiling of 10 per cent solutions of 1,1,3-triphenylbuta-

diene-1,2 in acetic acid or acetic anhydride, gave an isomer of m.p. 163° , probably 1,1,3-triphenylbutadiene-1,3.⁶⁷⁹

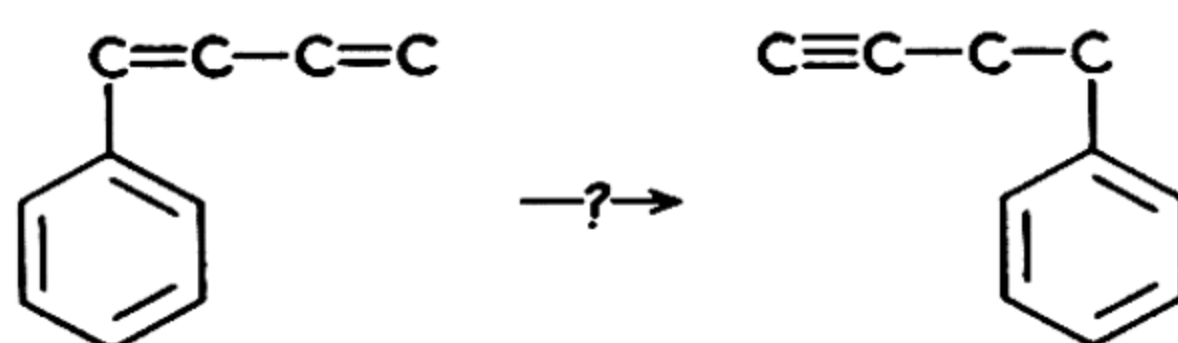


Non-Allenic Alkadienyl Benzenes

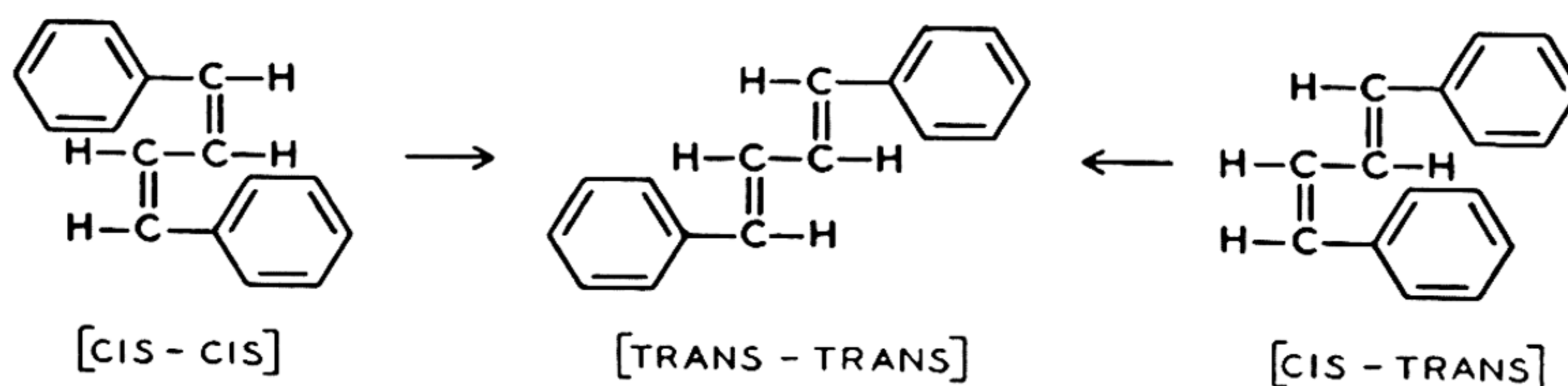
Cis-1-phenylbutadiene-1,3-isomerized completely into *trans*-1-phenylbutadiene-1,3 when allowed to stand overnight with a trace of hydrochloric acid, and then distilled:³⁹⁵



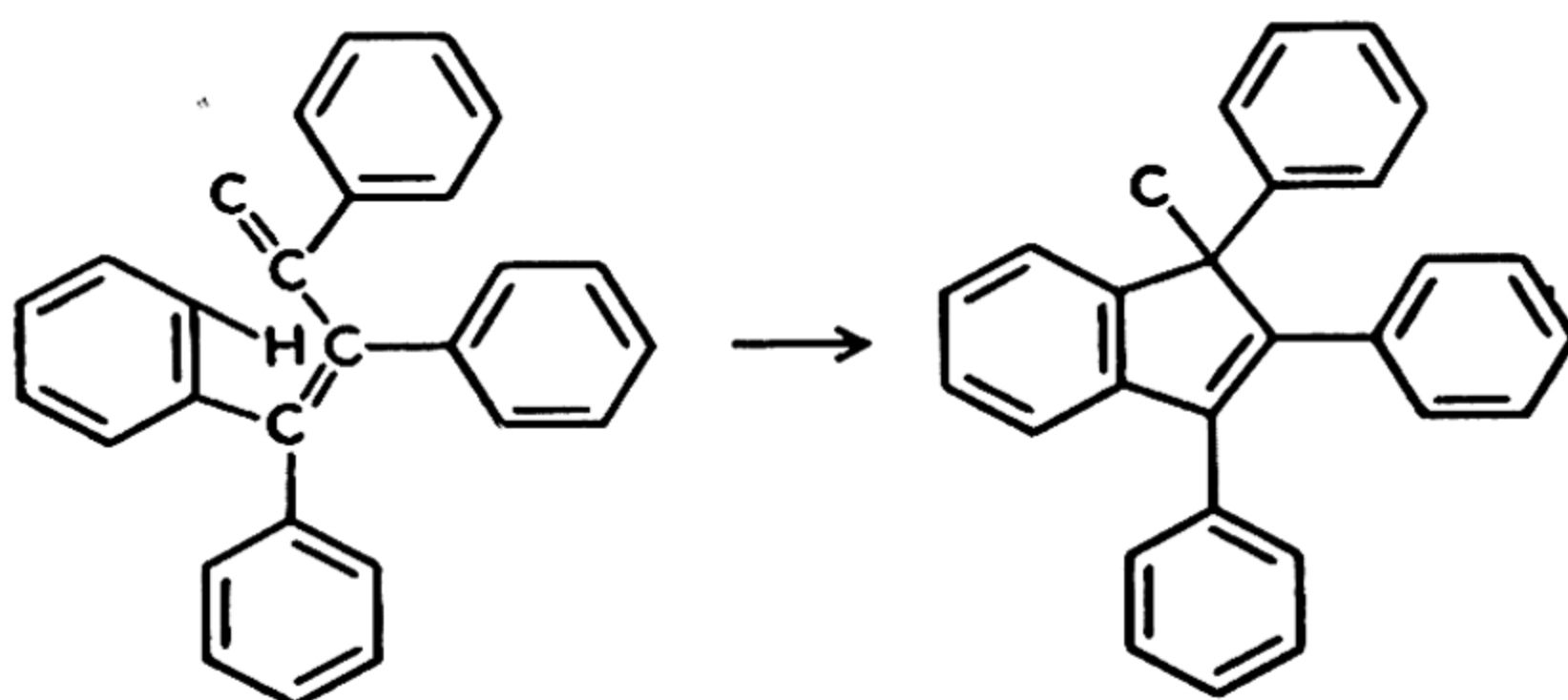
1-Phenylbutadiene-1,3, when passed over "Floridin" at $290-300^{\circ}$, gave probably 4-phenylbutyne-1, along with a large amount of polymer:⁵⁵⁵



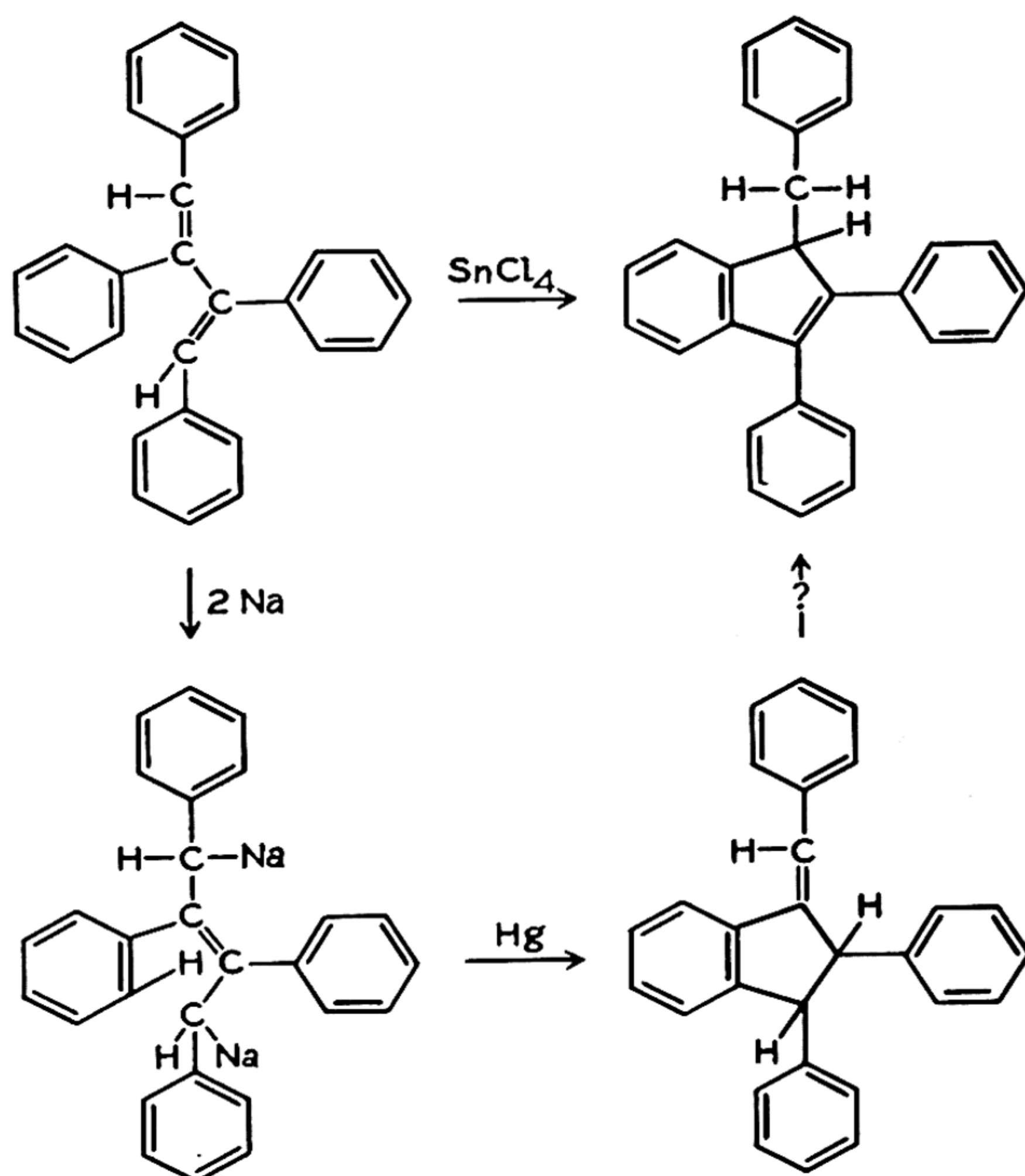
1,4-Diphenylbutadiene-1,3 is known in 3 geometrically isomeric forms: the stable *trans-trans* or α -form (m.p. 151°); the *cis-cis* or β -form (m.p. 70.5°), and the liquid *cis-trans* or γ -form.⁵⁷² The *cis-cis* and *cis-trans* forms isomerized into the stable *trans-trans* form upon exposure to sunlight:⁵⁷²



1,1,2,3-Tetraphenylbutadiene-1,3 yielded quantitatively 1-methyl-1,2,3-triphenylindene under the action of boiling acetic acid, containing a little sulfuric acid, for 5 minutes: ^{316a}



1,2,3,4-Tetraphenylbutadiene-1,3 was 60 per cent isomerized to 1-benzyl-2,3-diphenylindene when treated in benzene with stannic chloride.⁵⁷ Treatment in ether with sodium (for 3 days), followed by mercury, resulted in another isomer, that of 1-benzylidene-2,3-diphenylindane, and in 1-benzyl-2,3-diphenylindane plus 1,2,3,4-tetraphenylbutane.* The accepted course of the metalation-demetalation is a 1,4-addition of sodium, followed by the formation of 1-benzylidene-2,3-diphenylindane in the presence of mercury:



* The isomerization to 1-benzyl-2,3-diphenylindene, via stannic chloride in benzene, warrants an investigation of the benzylideneindanes. The latter should be capable of conversion into benzylindenes in the presence of "acidic" catalysts.

The experimental data on isomerizations of alkadienyl benzenes are given in Table 37, p. 378.

Conclusions

1. The allenic alkadienyl benzenes have been isomerized into: an alkynyl benzene, a racemic allenic alkadienyl benzene, a probably non-allenic phenylated alkadiene, indenenes, and several 3- α -naphthindenenes.

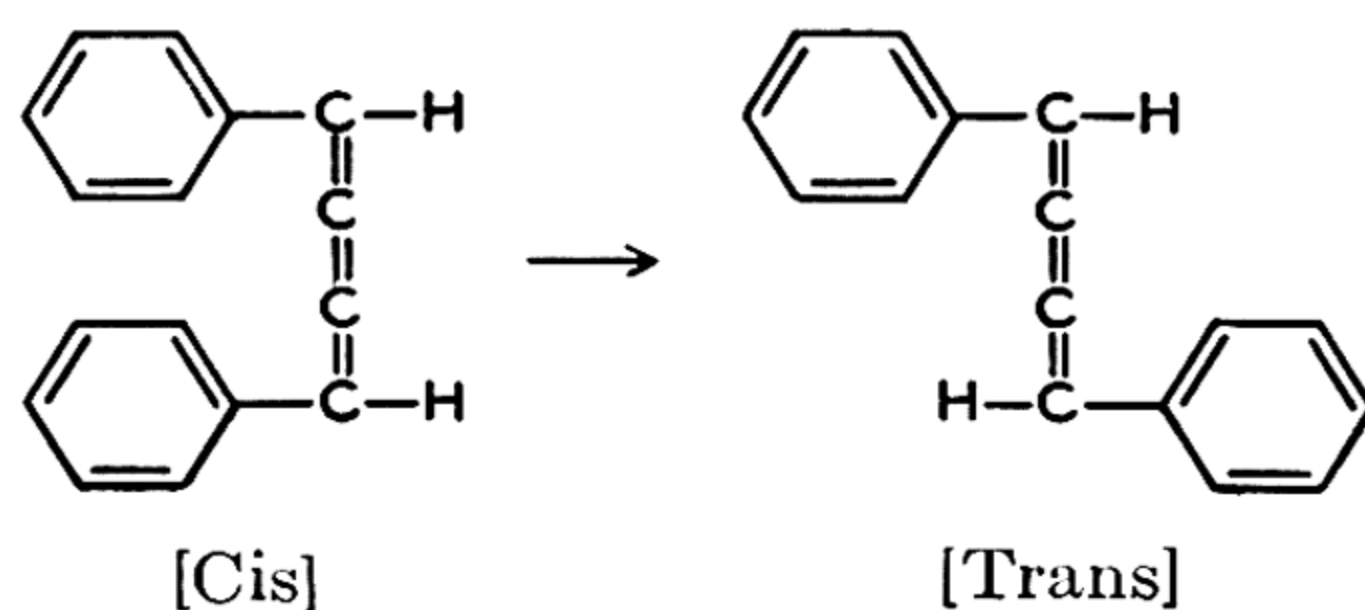
2. The use of acidic catalysts in the isomerization of allenic alkadienyl benzenes resulted in the formation of indenenes. Alcoholic potash as catalyst led to the formation of an alkyne, whereas boiling decalin was effective in causing a racemization.

3. Non-allenic, aromatic alkadienes were observed to change into stable *trans* forms, a probable alkynyl benzene, an indane, and indenenes.

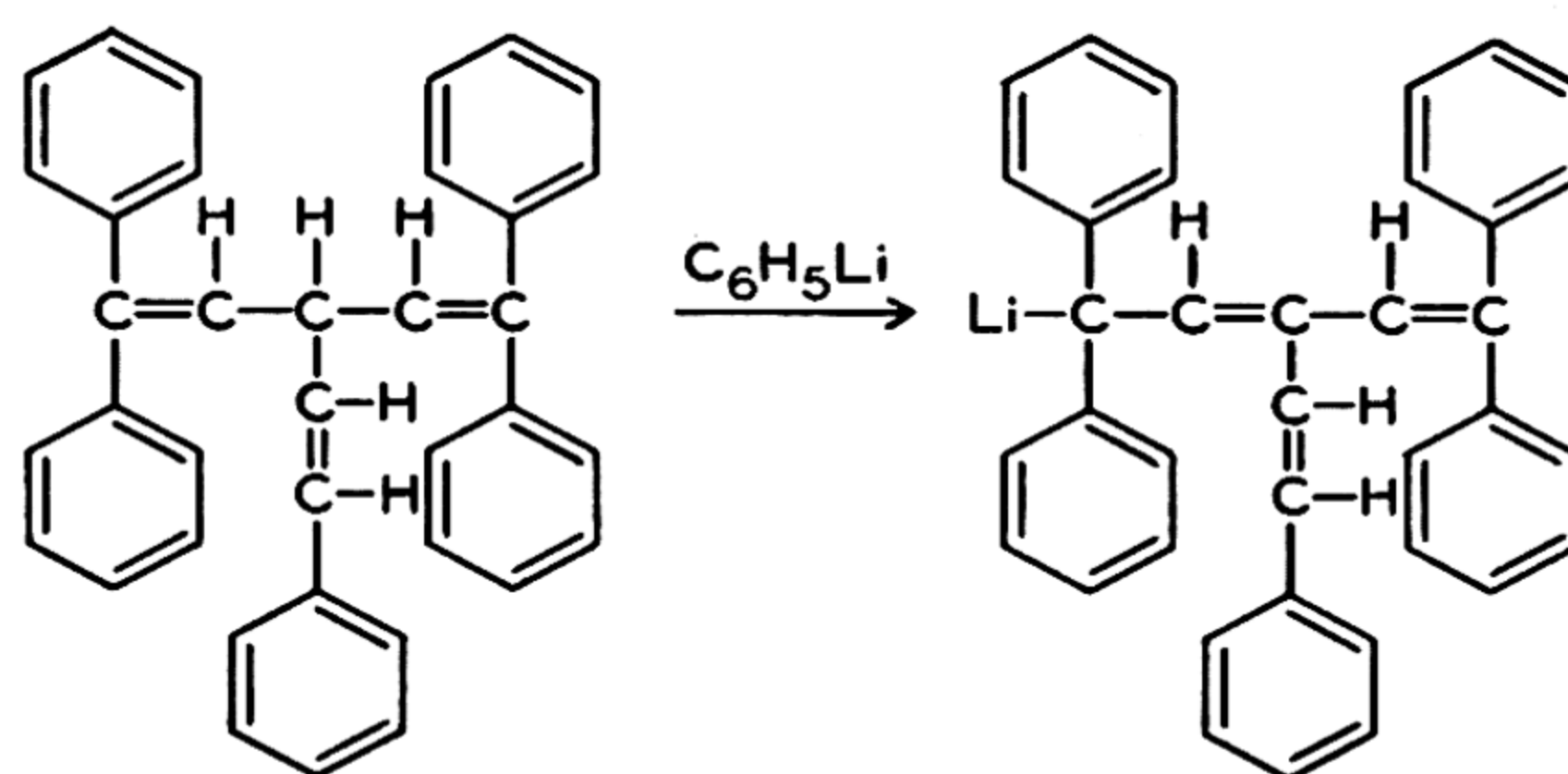
ALKAPOLYENYL BENZENES

Isomerizations

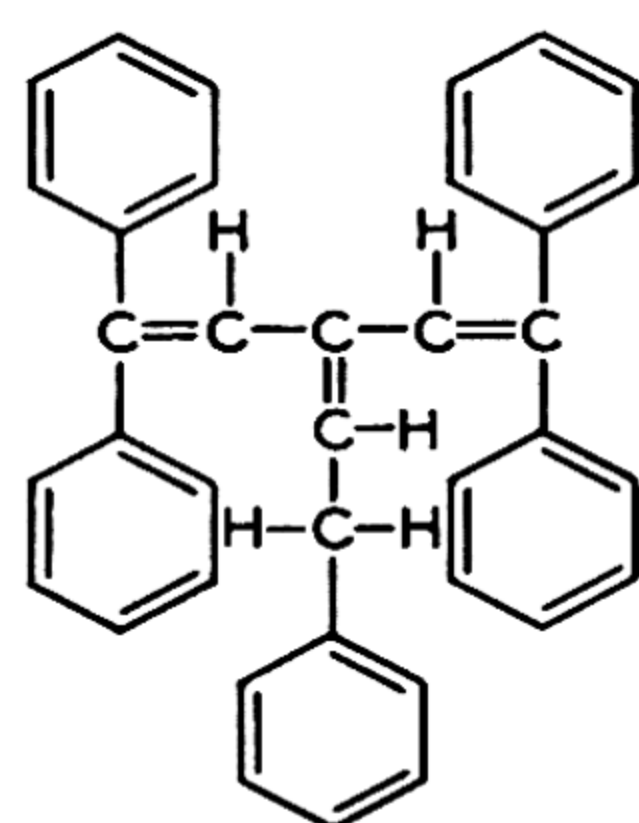
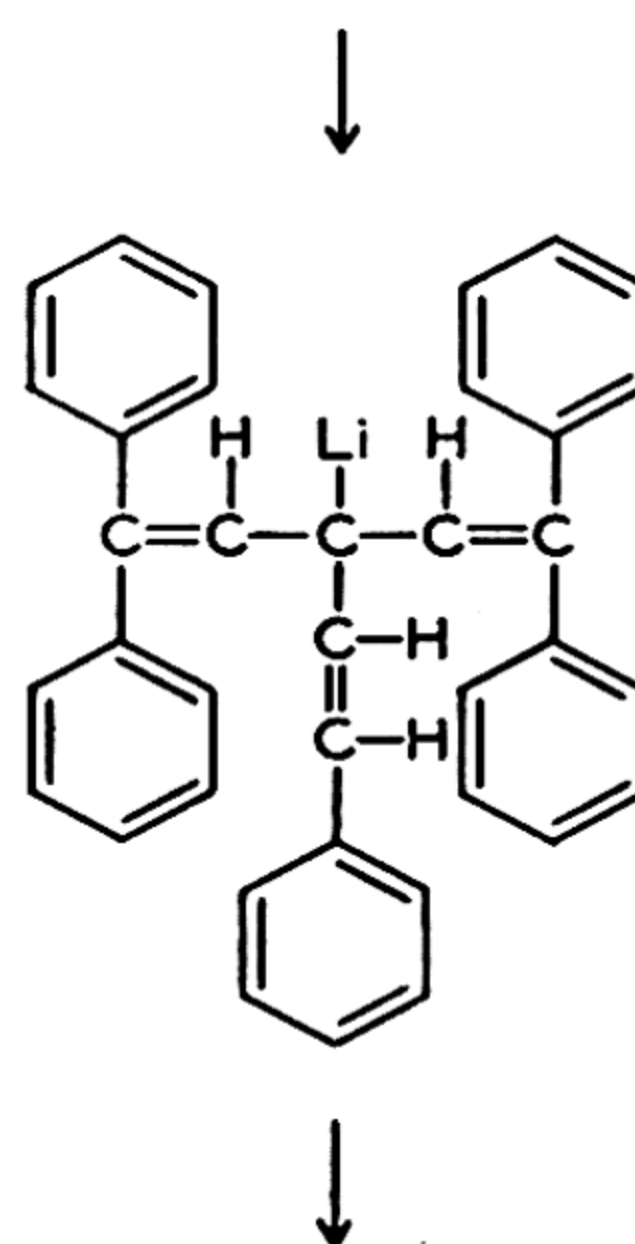
1,4-Diphenylbutatriene is known in two geometrically isomeric forms: the stable *trans* form (m.p. 97°), and the liquid or unstable *cis* form. Both forms were originally taken for the *cis* and *trans* forms of 1,4-diphenylbutenyne,⁵⁷² but this is untenable when viewed from the standpoint that an exclusive formation of benzaldehyde occurs on oxidation.²²⁹ On prolonged exposure to sunlight, the *cis* form isomerized to the stable *trans* form,^{229, 572} especially when traces of iodine were present:⁵⁷²



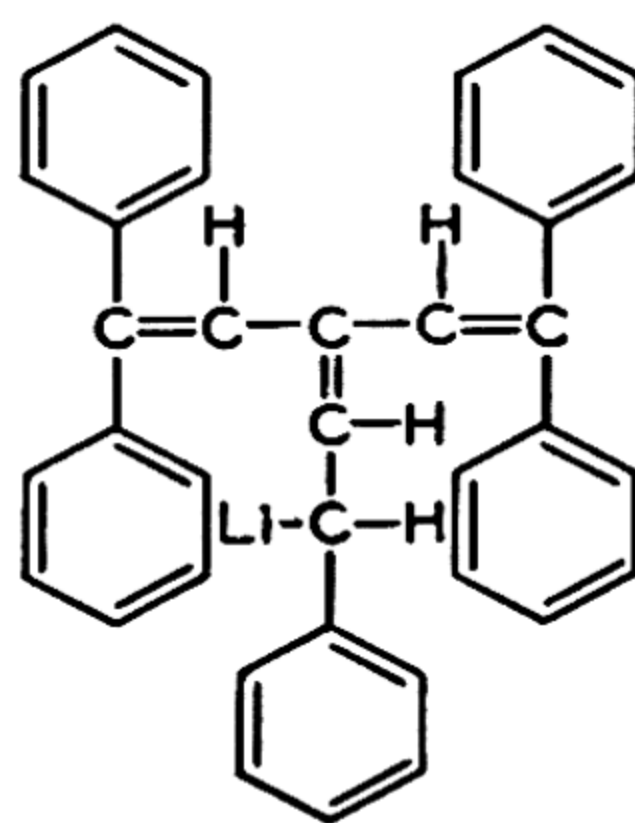
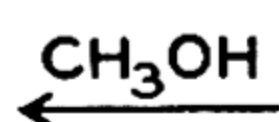
1,1,5,5-Tetraphenyl-3-styrylpentadiene-1,4 [*i.e.*, styrylbis (β,β -diphenylvinyl) methane], when treated with phenyl-lithium, gave a precipitate of a lithium derivative. The latter was then alcoholized, by an excess of methanol, into an isomer of the initial hydrocarbon: 1,1,5,5-tetraphenyl-3-phenethylidene-pentadiene-1,4 (*i.e.*, phenyl- $[\beta,\beta$ -bis(β,β -diphenylvinyl) vinyl]methane or 1-benzyl-2,2-bis $[\beta,\beta$ -diphenylvinyl]-ethylene of m.p. 130-131°).⁶⁵⁴ The following triple “allyl tautomerism” was given as an explanation of the foregoing isomerization:⁶⁵⁴



1,1,5,5-Tetraphenyl-3-styrylpentadiene-1,4

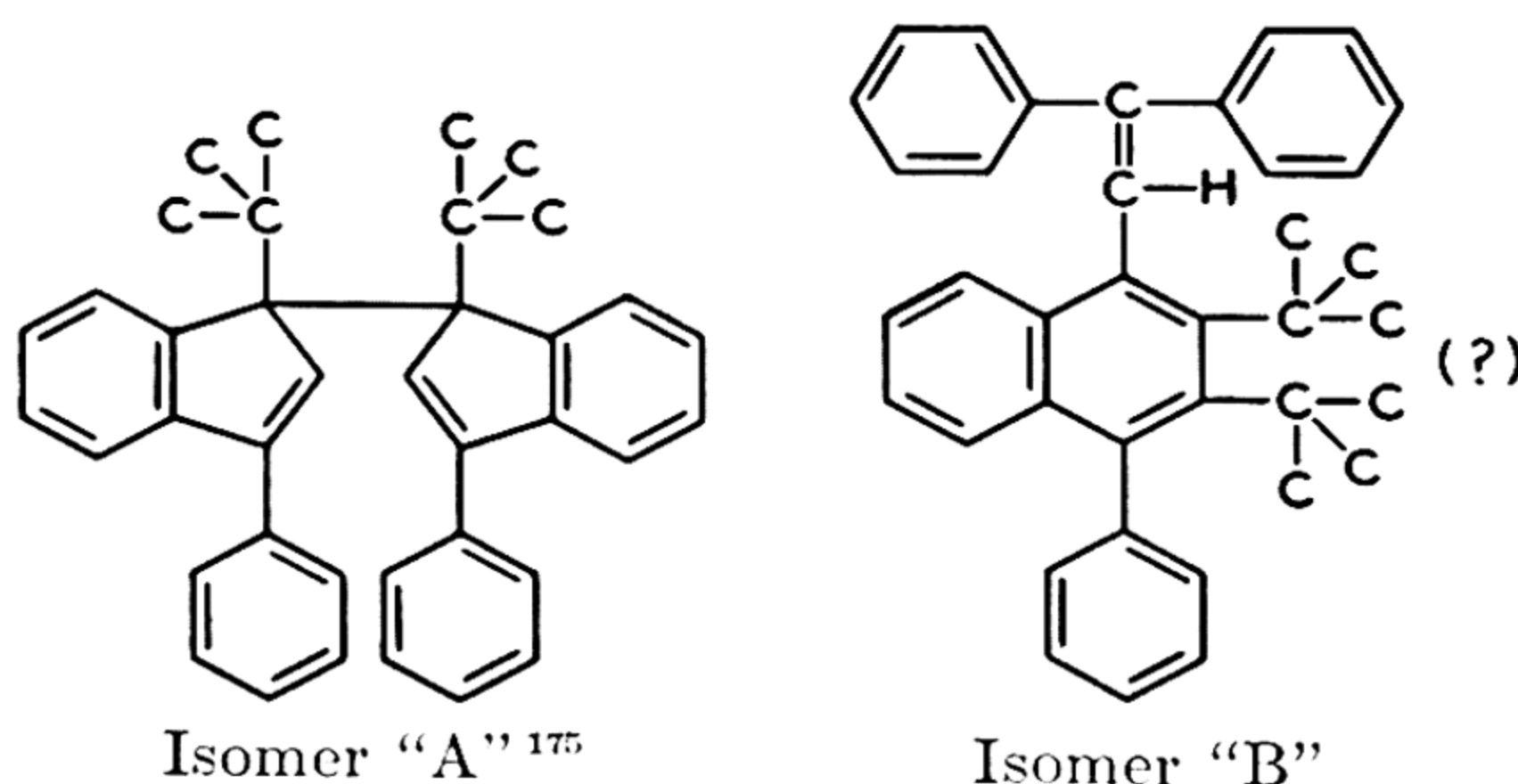
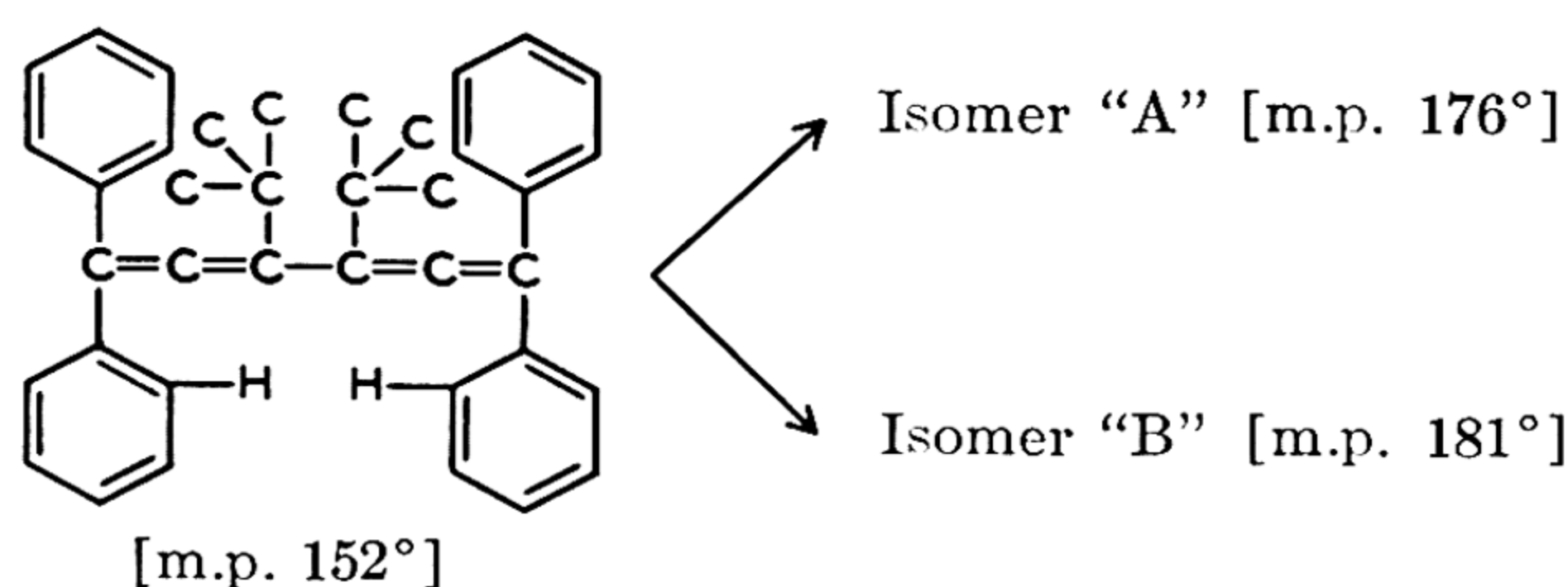


1,1,5,5-Tetraphenyl-3-phenylethylidene-pentadiene-1,4



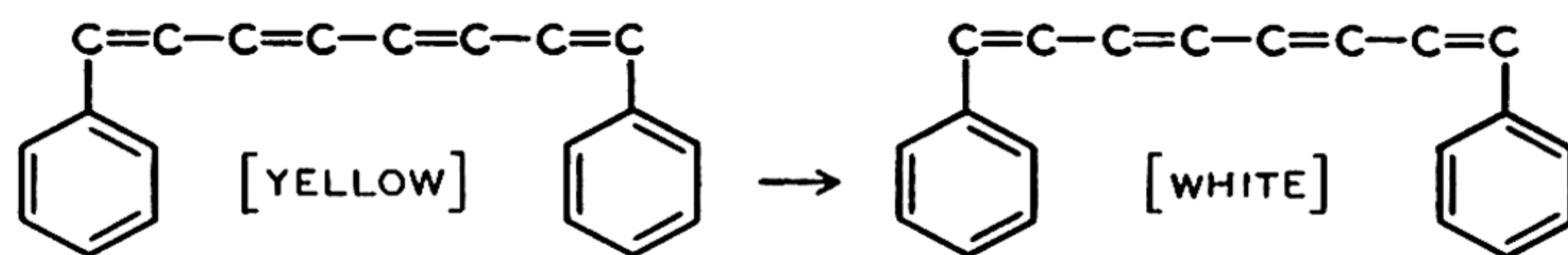
If one assumes the formation of the symmetrical lithium derivative as the logical first step of the isomerization, then the process is shortened into a simple "allyl transformation."

1,1,6,6-Tetraphenyl-3,4-di-*tert*-butyl-hexatetraene-1,2,4,5 (a diallenyl of m.p. 152°), upon treatment with acetic acid plus hydrogen chloride, was isomerized by a double cyclization to 1,1'-di-*tert*-butyl-3,3'-diphenyl-1,1'-biindene (the diindenyl "A" of m.p. 176°).^{3, 175} However, the reports of one group of investigators,³ in which the diallenyl (m.p. 152°) has been mistaken for the diindenyl, have caused considerable confusion. Later workers¹⁷⁵ proposed the diindenyl structure for the isomer of m.p. 176° . Recently,³⁶⁰ it was stated that this isomer "A" cannot be the diindenyl. The arguments^{217, 240, 360} are unconvincing, since they apply rather to the related 1,1',3,3'-tetraphenyl-1,1'-biindene that theoretically should occur in meso and racemic forms (the existence of these forms was not proved). Treatment of the diallenyl (m.p. 152°) with sodium amalgam in the presence of ether gives still another isomer "B" (m.p. 181°) of unknown structure.^{3, 175, 360} It has been suggested that the isomer "B" may be a substituted naphthalene.³⁶⁰ The ultraviolet absorption spectra of isomers "A" and "B" showed no similarity with that of 2,8-diphenyl-6b,12b-dihydrochrysene and 2,8-diphenylchrysene. This fact was taken as evidence that "A" and "B" are not substituted 6b,12b-dihydrochrysenes.³⁶⁰



1,8-Diphenyloctatetrene-1,3,5,7 exists in two stereo-isomeric forms: colorless (m.p. 124°)¹⁸⁴ and yellow (m.p. 225°).¹⁹⁰ The yellow form, when dissolved in chloroform containing free iodine and exposed to sun-

light for several days (in an atmosphere of carbon dioxide), gave the white form and a resin.⁵⁶⁶ Similar results were obtained when the yellow solid was exposed to sunlight for 3 months in the presence of carbon dioxide. The reaction is apparently not reversible:



Isomerizations of alkapolyenyl benzenes are presented in Table 38, p. 380.

Conclusions.

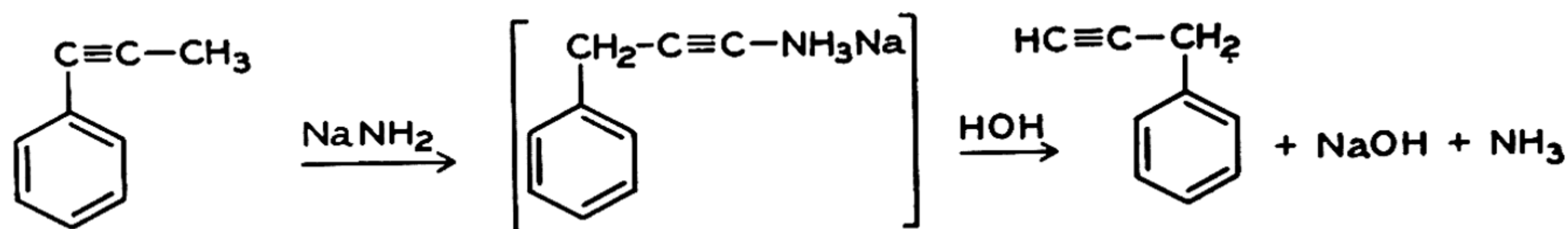
1. The alkapolyenyl benzenes exhibit several types of isomerization. The simpler changes comprise the conversion of a *cis* into the corresponding *trans* form, and the formation of a phenethylidene group from its styryl analog.

2. Cyclization in several directions is a factor that makes the study of one diallenyl difficult.

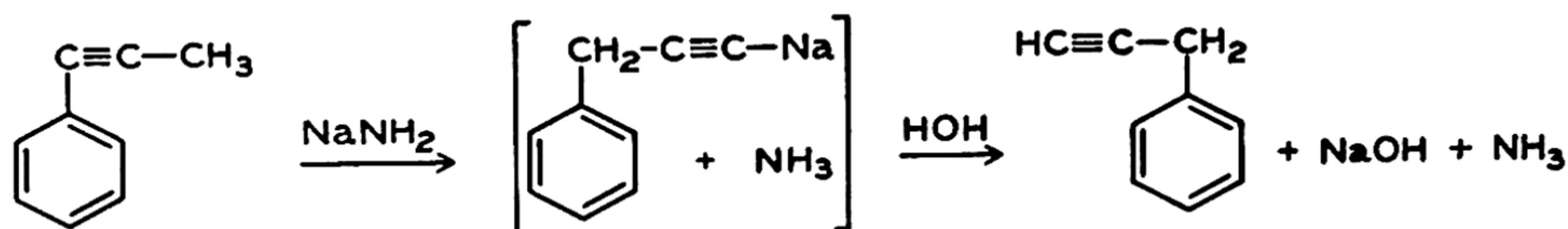
ALKYNYL BENZENES

Isomerizations

1-Phenylpropyne-1 under the action of sodamide at 110° for 2 hours (with toluene as diluent), followed by hydrolysis of the intermediary organosodium derivative, was isomerized into 3-phenylpropyne-1.^{80, 81} This reaction apparently proceeds as follows: ⁸²

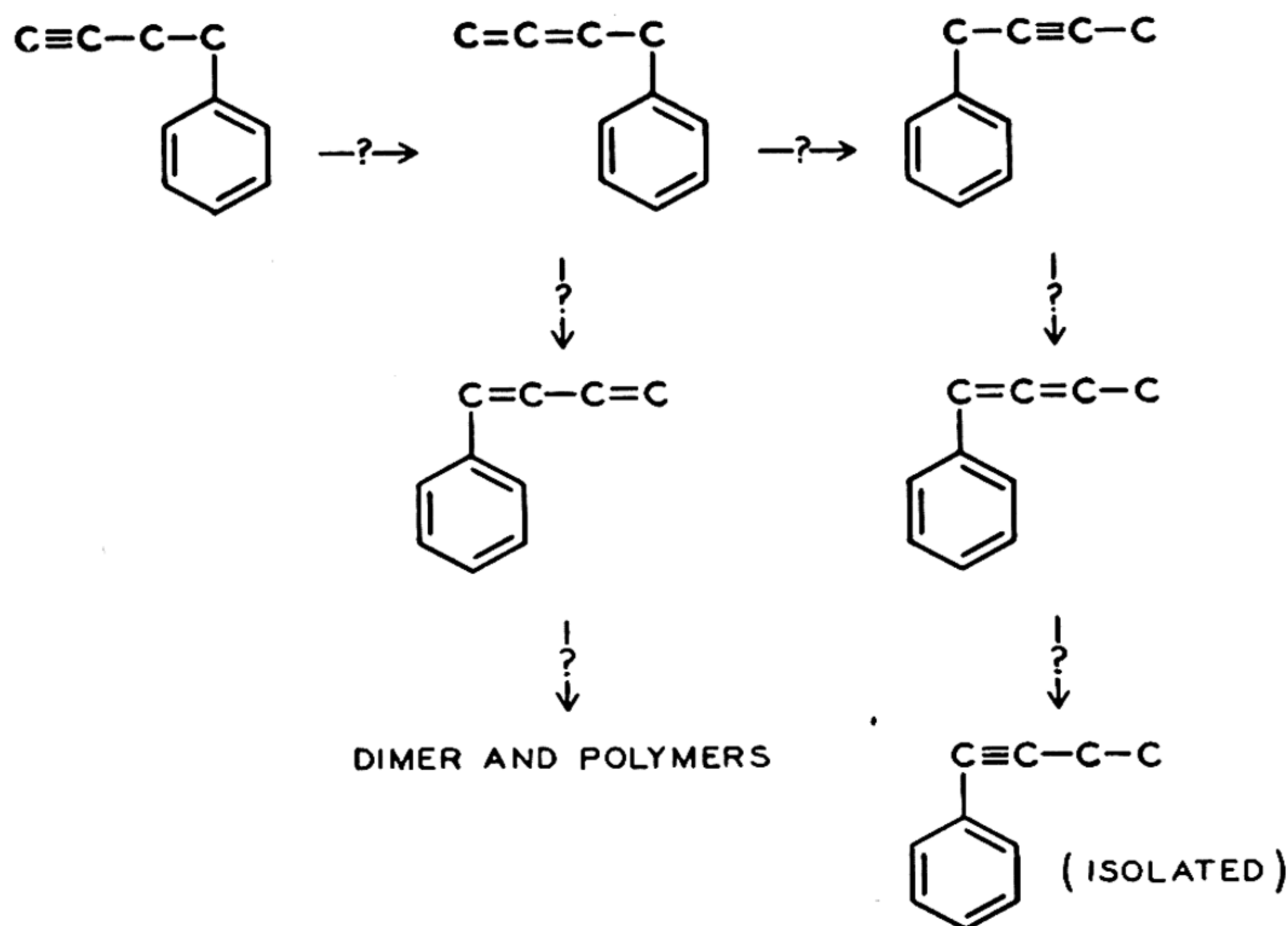


Intermediary formation of sodium benzylacetylide plus ammonia serves as alternative explanation of this isomerization:



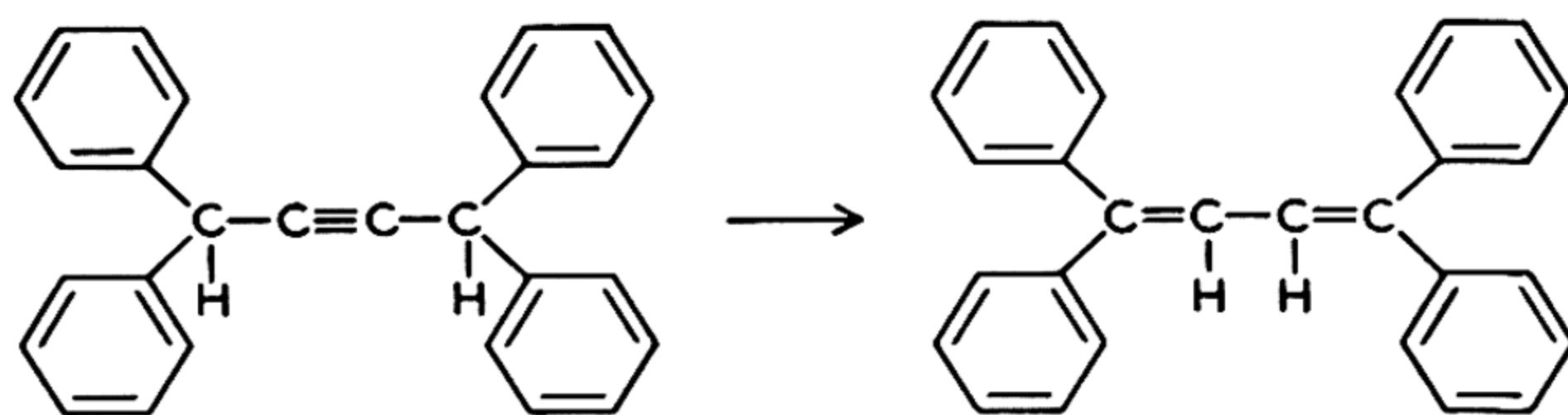
4-Phenylbutyne-1 formed less than 25 per cent of 1-phenylbutyne-1 and 75 per cent of polymers upon passage over chromia at 250° in a stream of carbon dioxide.^{344a} The course of the isomerization was con-

sidered to be successive formations of 4-phenylbutadiene-1,2, 1-phenylbutyne-2, 1-phenylbutadiene-1,2, and 1-phenylbutyne-1; conversion of 4-phenylbutadiene-1,2 into 1-phenylbutadiene-1,3 would account for the extensive polymerization:

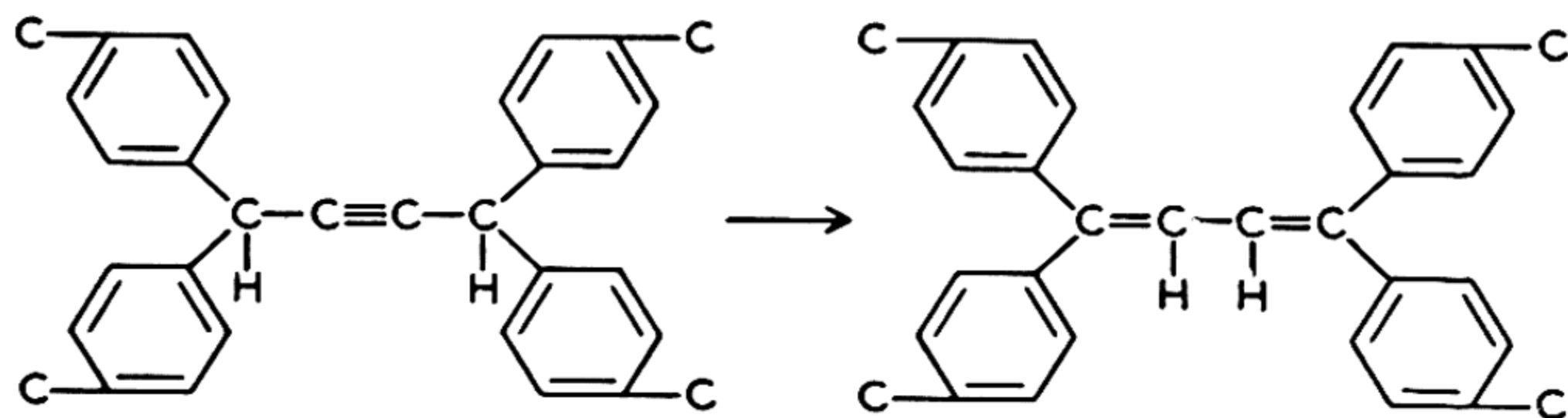


4-Phenylbutyne-1 when passed over "Floridin" at 250° probably yielded a small amount of 4-phenylbutadiene-1,2, *i.e.*, benzylallene.⁵⁵⁵

1,1,4,4-Tetraphenylbutyne-2, heated with alcoholic sodium ethoxide, was converted into 1,1,4,4-tetraphenylbutadiene-1,3: ^{84, 85}

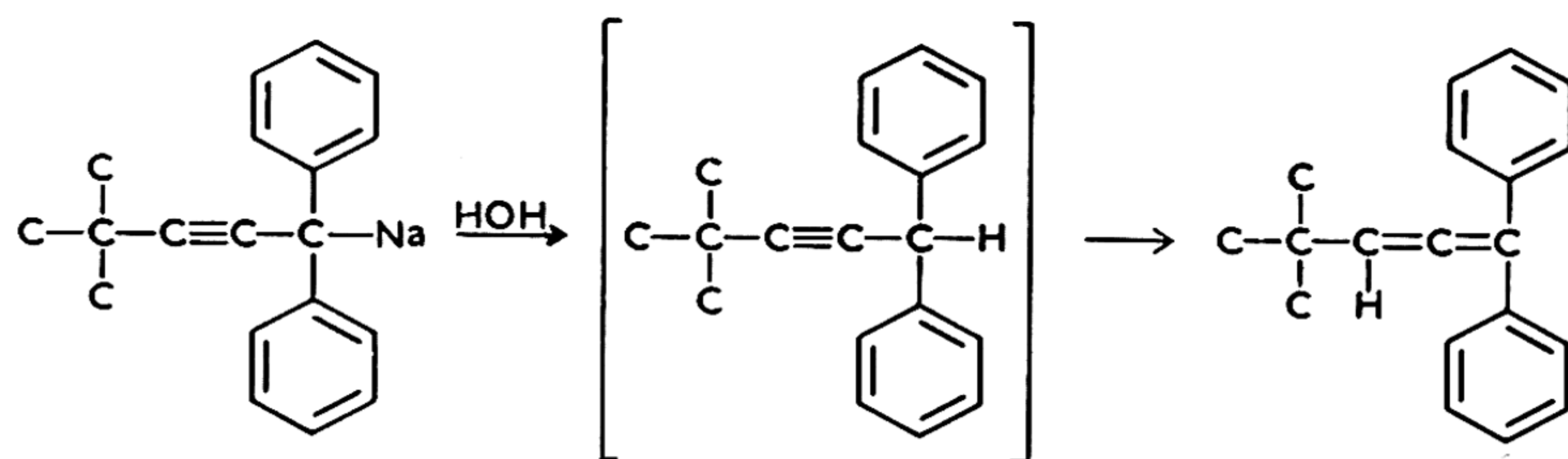


1,1,4,4-Tetra-*p*-tolylbutyne-2, heated under reflux for 3 hours with alcoholic sodium ethoxide, was isomerized to 1,1,4,4-tetra-*p*-tolylbutadiene-1,3: ⁸⁶



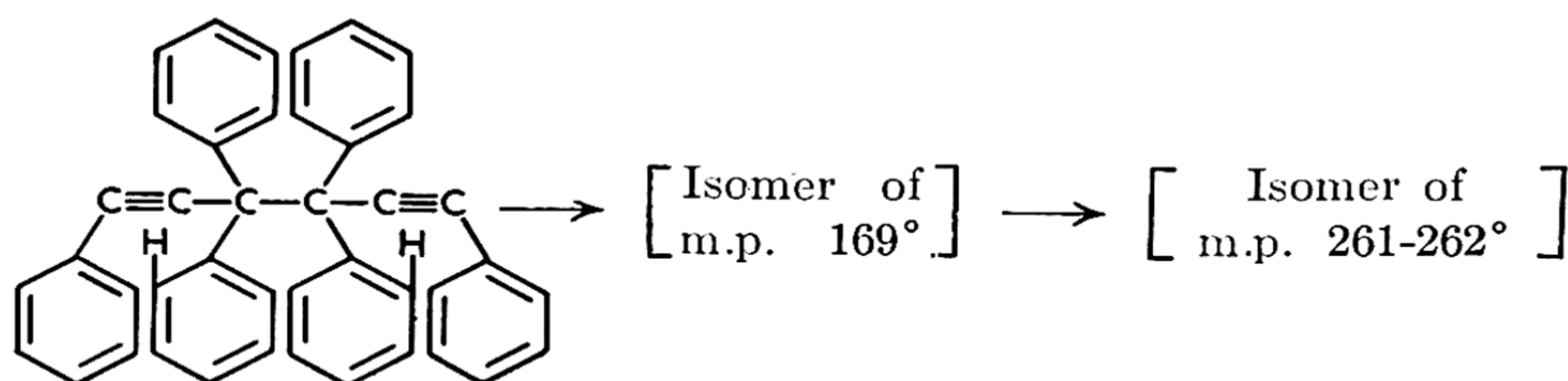
Treatment of 2,2,9,9-tetramethyl-5,5,6,6-tetraphenyldecadiyne-3,7 (*i.e.*, 1,2-di-*tert*-butylethynyl-tetraphenylethane) with 40 per cent

sodium-amalgam yielded diphenyl-*tert*-butylethynylmethylsodium (*i.e.*, a pentyne derivative). Hydrolysis⁵⁶⁴ of this organosodium compound gave an allene, probably via the corresponding alkyne. This reaction is of interest in connection with the theory of isomerization of aliphatic allenes and alkynes. The present non-formation of an alkyne-1 (with sodium amalgam as "catalyst") is due to an interference in hydrogen migration (a blocking caused by presence of specific methyl and phenyl groups):



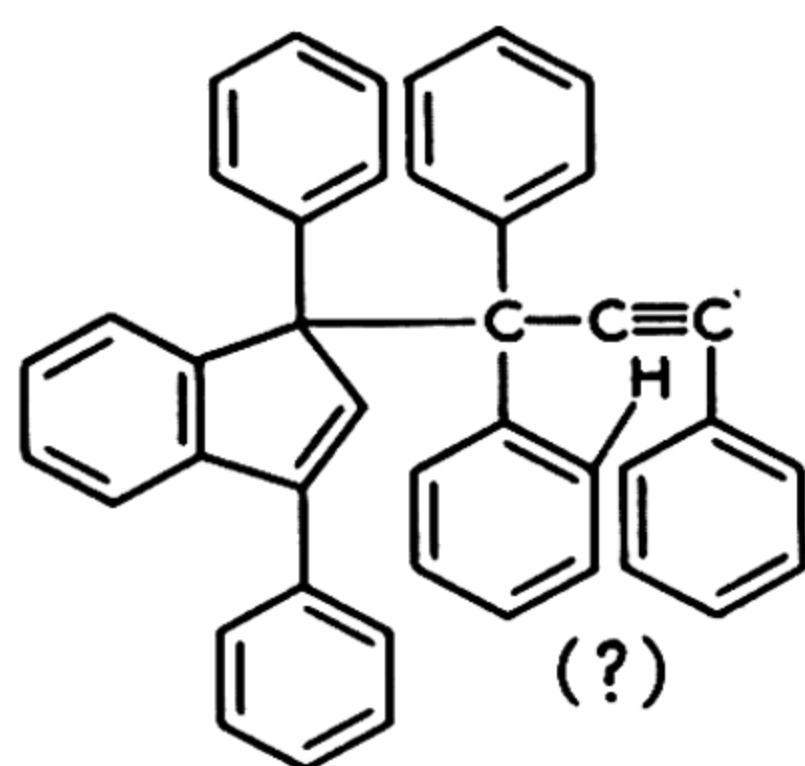
(Compare this scheme with the shift of a methyl group within 4,4-dimethylpentadiene-1,2).

1,3,3,4,4,6-Hexaphenylhexadiyne-1,5 (in petroleum ether) was converted in one hour at room temperature into an isomer of unknown structure (m.p. 169° when "pure").³⁹³ The new isomer was found to be identical with a hydrocarbon (m.p. 179°) obtained by the coupling of phenethynyl(diphenyl)methyl.³⁸⁹ The hydrocarbon of m.p. 179°, however, was erroneously considered to be 1,3,3,4,4,6-hexaphenylhexadiyne-1,5. A sample of the foregoing coupled-hydrocarbon (m.p. 172-173°), when boiled with acetic acid saturated with hydrogen chloride, gave still another isomer of unknown structure (m.p. 261-262°).²⁴⁰ Knowledge of the course of these isomerizations is limited; they apparently involve two successive cyclizations:

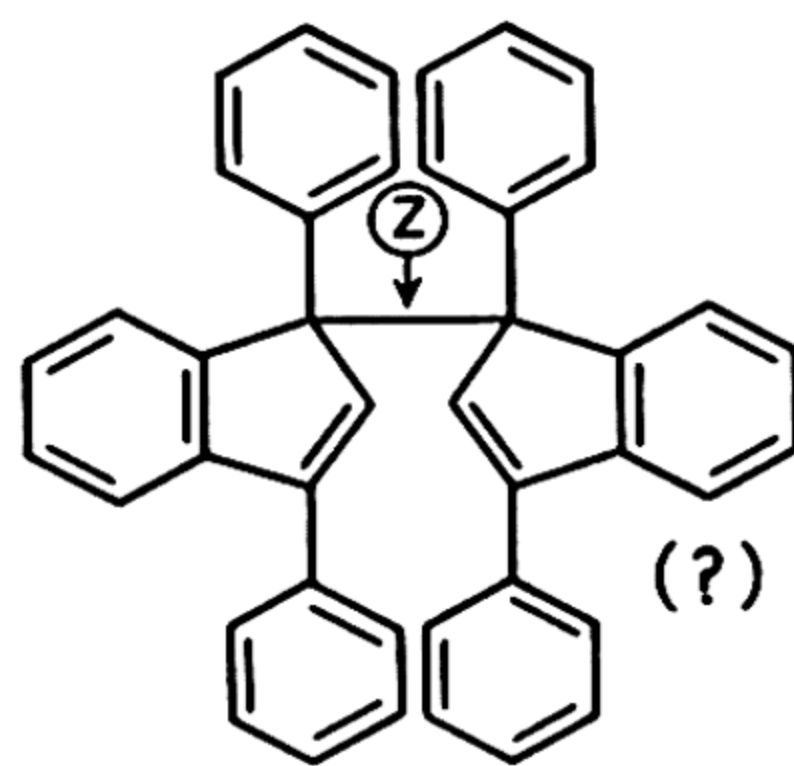


1,3,3,4,4,6-Hexaphenylhexadiyne-1,5

The isomer of m.p. 169° [179°, 172-173°] may have the structure of 1-(1,1,3-triphenylpropargyl)-1,3-diphenylindene, whereas the isomer with m.p. 261-262° is probably 1,1',3,3'-tetraphenyl-1,1'-biindene [*i.e.*, bis-1,1'-(1,3-diphenylindenyl)]:



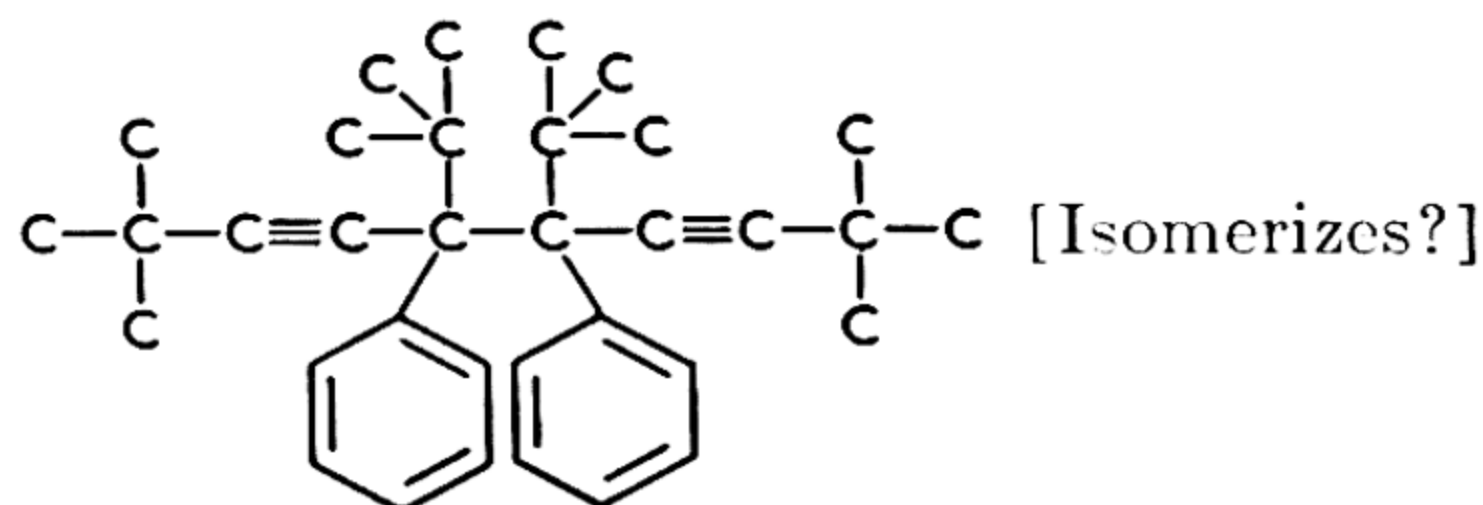
[Isomer of m.p. 169°]



[Isomer of m.p. 261-262°]

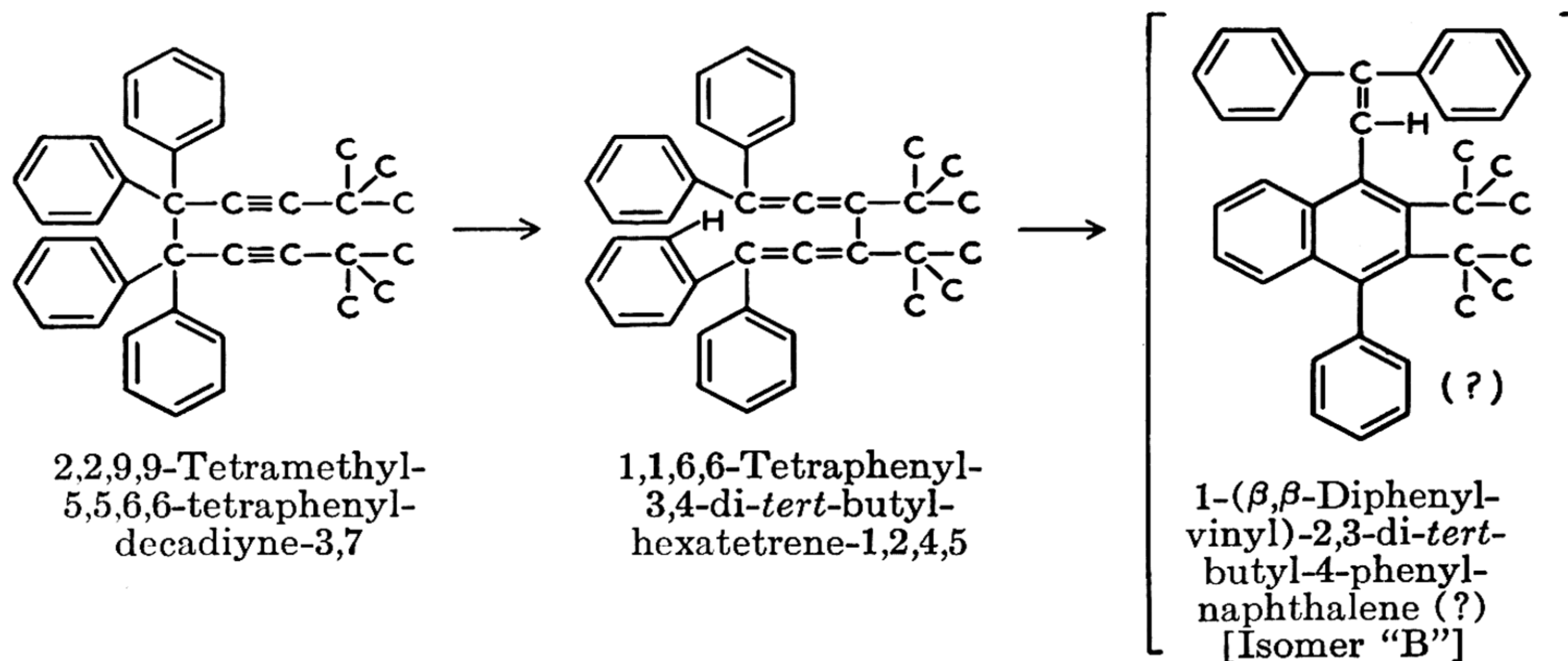
The opinion has been expressed²⁴⁰ that the isomers (m.p. 169° and 261-262°) cannot be the substituted-diindenyl (*i.e.*, 1,1',3,3'-tetraphenyl-1,1'-biindene). The arguments^{217, 240} supporting this opinion are unconvincing, since the substituted diindenyl (synthesized) dissociates readily. Moreover, the position of the diyl bridge "Z" (*infra*) in the supposed true synthetic (m.p. 190-191°) remains unproved to date. Another investigator⁶⁴⁸ considers the corresponding monoindenyl structure to be more plausible for the m.p. 261-262° isomer than the diindenyl formula, disregarding the fact that the "indene" is a precursor of the "diindenyl." The recent synthesis of a substituted 6b,12b-dihydrochrysene³⁶⁰ suggests an investigation of the isomerization products for the presence of 2,6b,8,12b-tetraphenyl-6b,12b,-dihydrochrysene. On the other hand, one should not overlook the possible presence of tetraphenyldihydronaphthacene-related hydrocarbons, which have been emphasized in the coupling of substituted triethynylmethyl halides.⁵⁶² The isomer of m.p. 179°, when heated in xylene solution with various oxidizing substances,⁶⁴⁸ or merely fused,^{389, 647} gave a yellow isomer with m.p. 225°⁶⁴⁸ or 249°.⁶⁴⁷

A possible although unreported isomerization of 2,2,9,9-tetramethyl-5,6-di-*tert*-butyl-5,6-diphenyldecadiyne-3,7 (*i.e.*, 1,2-di-*tert*-butyl-1,2-di-*tert*-butylethynyl-diphenylethane) into a stable isomer may occur in the reaction between (*tert*-butyl) (*tert*-butylethynyl) (phenyl) methyl bromide and sodium amalgam (in the presence of ether).¹⁹²

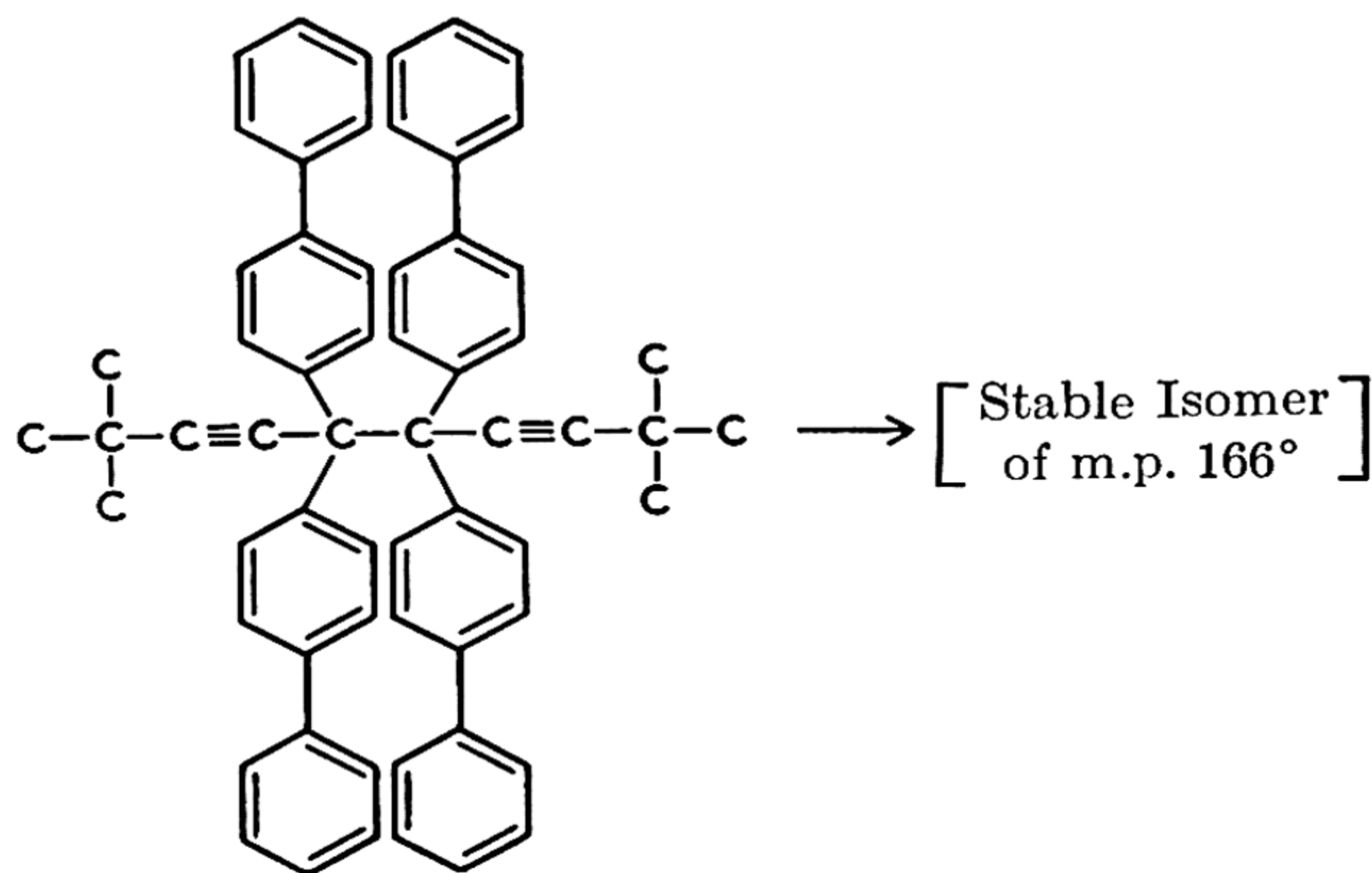


2,2,9,9-Tetramethyl-5,5,6,6-tetraphenyldecadiyne-3,7 (*i.e.*, 1,2-di-*tert*-butylethynyl-tetraphenylethane), upon standing at room temperature in ether, was isomerized to the diallenyl, 1,1,6,6-tetraphenyl-3,4-di-*tert*-butyl-hexatetrene-1,2,4,5 (m.p. 153°). This reaction was completed

within 12 hours, but when the ethereal solution was heated to 50° , the isomer was formed in a few minutes.⁵⁶⁴ Acetone, hexane, and heptane can be used also as solvents. The structure of the isomer is given in a recent publication.¹⁷⁵ Treatment⁵⁶⁴ of 1,2-di-*tert*-butylethynyl-tetra-phenylethane with ether plus one per cent sodium-amalgam for several days, followed by alcohol, gave an "impure isomer" that probably was a mixture³ of the diallenyl (m.p. 153°) and its isomer "B" (m.p. 181°) encountered in the previous section on "Alkapolyenyl Benzenes":

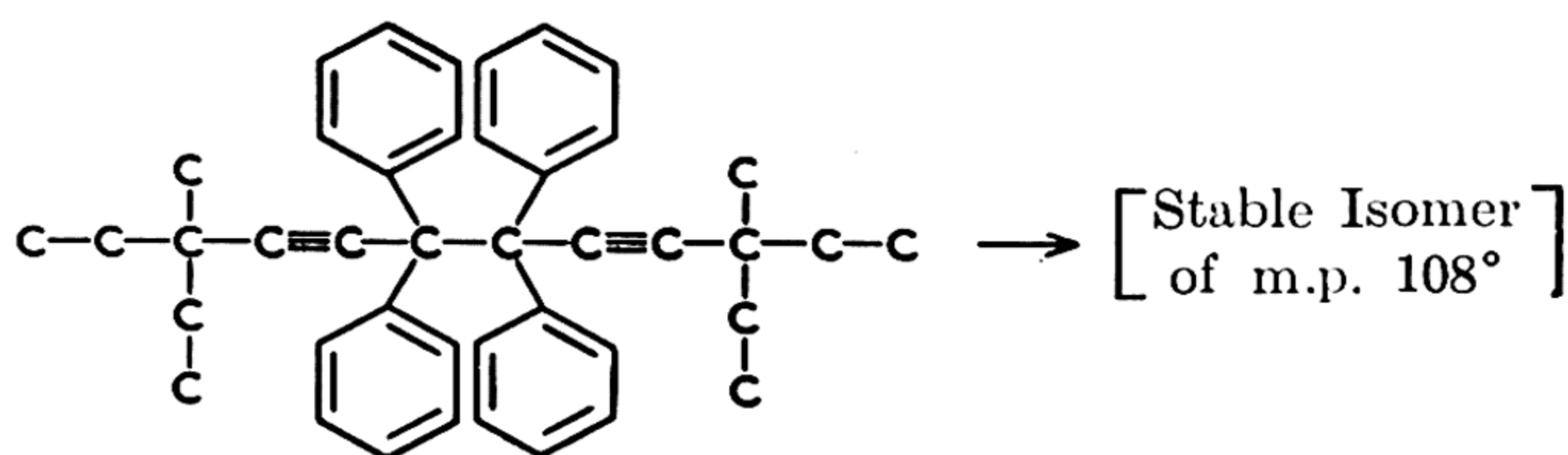


2,2,9,9-Tetramethyl-5,5,6,6-tetra-biphenyldecadiyne-3,7 (*i.e.*, 1,2-di-*tert*-butylethynyl-tetra-biphenylethane) was converted into an isomer (m.p. 166°) upon standing in toluene at room temperature for 10 hours.⁵⁹² The structure of the isomer is unknown. Half of the molecule probably retains its original carbon skeleton, since a 50 per cent yield of di-biphenyl ketone results upon oxidation of the new isomer by oxygen:



3,10-Dimethyl-3,10-diethyl-6,6,7,7-tetraphenyl-dodecadiyne-4,8 [*i.e.*, 1,2-di-(3-methyl-3-ethylpentynyl-1)-tetraphenylethane] isomerized at 0°

in a short time without a solvent, or at room temperature in the presence of ether.²⁴² The structure of the isomer is unknown, but there is some evidence that half of the molecule retains its original carbon skeleton:²⁴²



Isomerizations of alkynyl benzenes are presented in Table 39, p. 382.

Conclusions

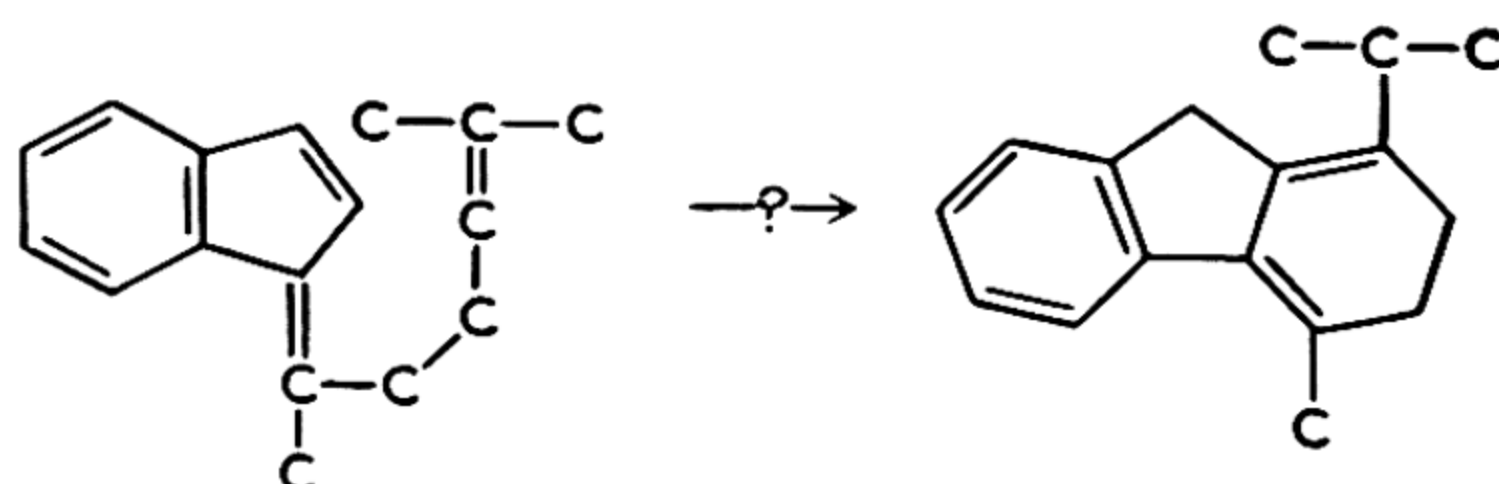
1. Alkynyl benzenes isomerize by hydrogen transfers, the extent of which varies considerably depending on the initial isomer.
2. 1,2-Di-*tert*-butylethynyl-tetraphenylethane exhibits no evidence of labile hydrogen activity in the presence of ether. However, when treated with sodium amalgam plus water, it forms an allenic scission product containing a hydrogen atom derived from the water.
3. Isomerizations of aryl propyne and of aryl butynes involve the migration of two hydrogen atoms.

CONDENSED AROMATICS

The condensed aromatic hydrocarbons comprise members of the indenes, fluorenes, naphthalenes, anthracenes, phenanthrenes, naphthalenes, and other fused-polycyclic systems. These members are discussed in the enumerated order. Isomerizations of more complex indenes are presented in the section on "Aromatic-Cyclene Hydrocarbons."

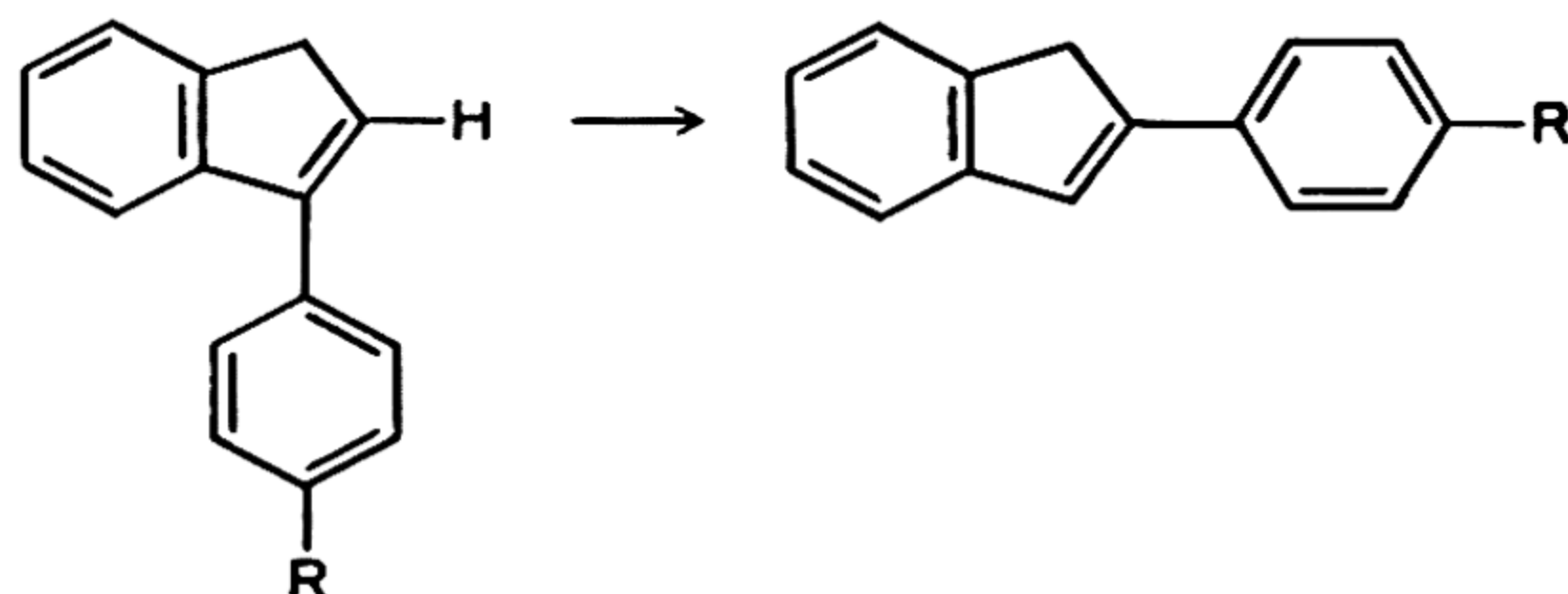
Indanes and Indenes

1-(1,5-Dimethyl-4-hexenylidene) - indene (*i.e.*, "methylisohexenyl-benzofulvene"), when heated at 140° for 12 hours with formic acid, gave a tricyclic isomer, probably 1-isopropyl-4-methyl-2,3-dihydrofluorene:⁴⁹¹

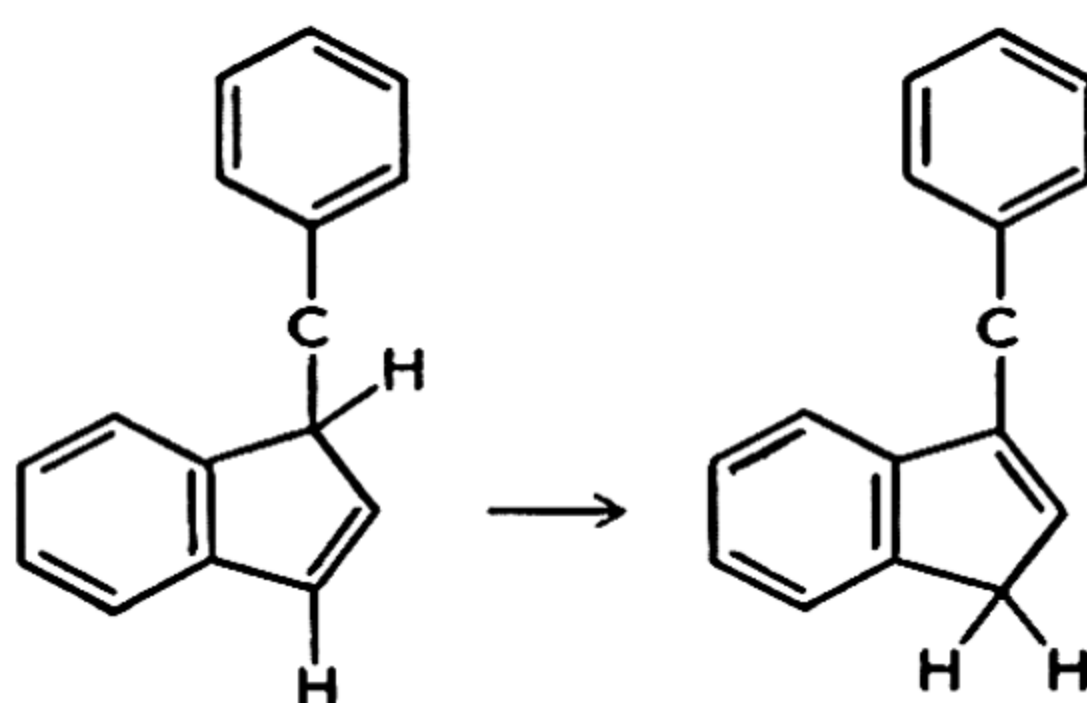


3-Phenylindene and 3-*p*-tolylindene, passed as vapors in a carbon dioxide atmosphere over punice heated to a dark-red heat (16 mm. Hg

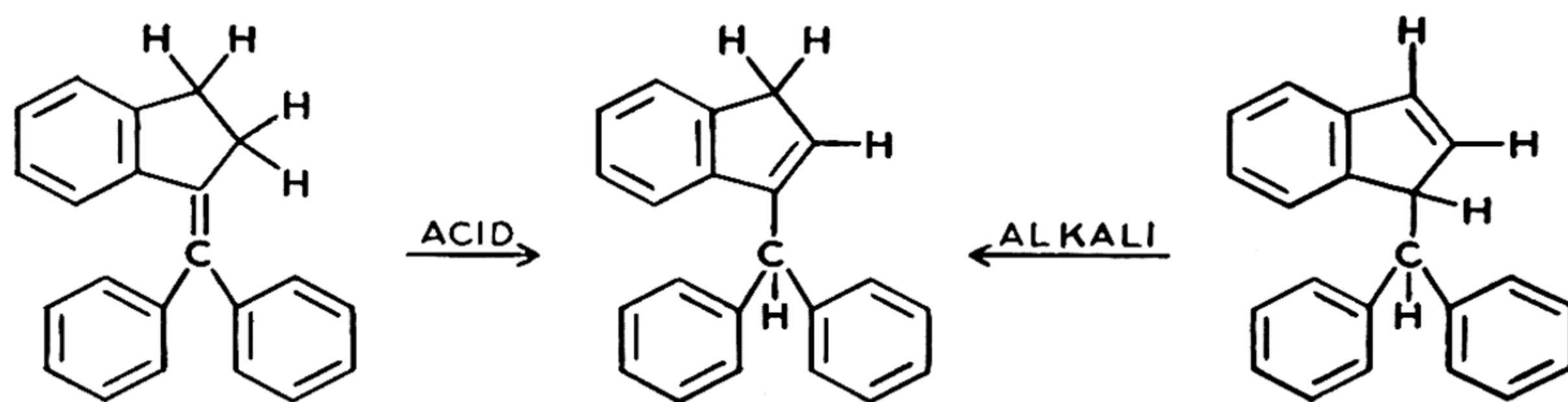
pressure), gave the 2-derivatives in yield of 33 and 16.5 per cent, respectively ⁸⁸ ("R" is H or CH₃):



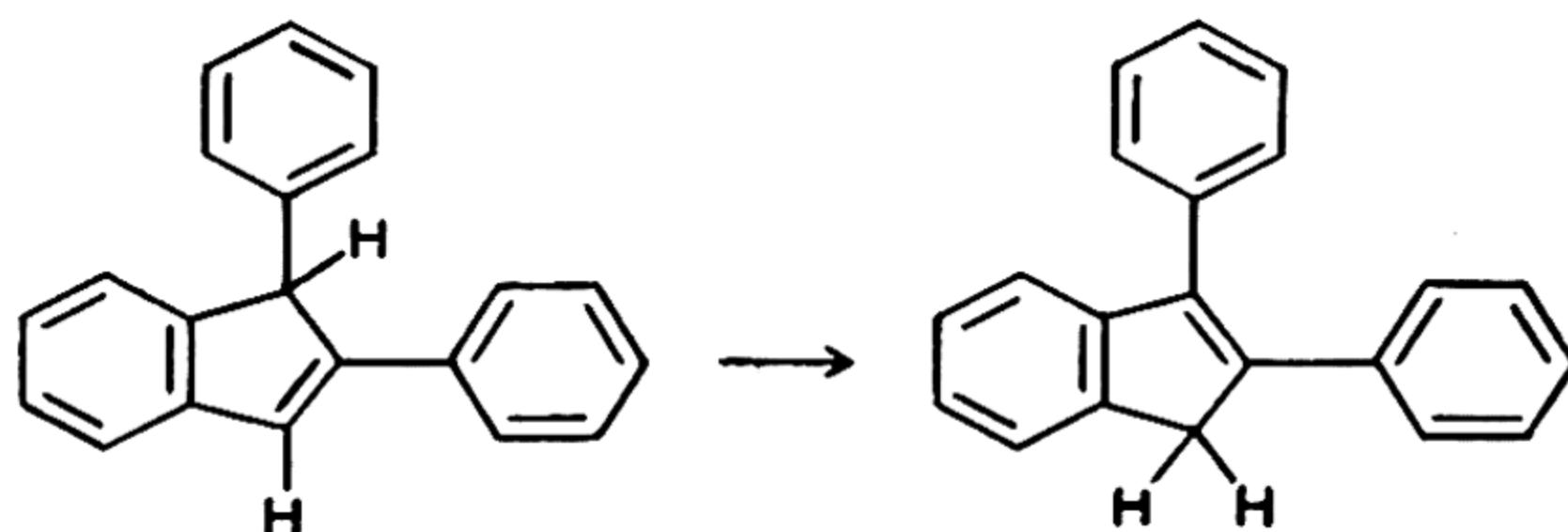
1-Benzylindene, upon treatment with potassium methoxide solution, gives 3-benzylindene.^{126, 127} This isomerization involves obviously only an allylic-type of hydrogen migration, regardless of the confusion caused by a change in numbering from 1- to 3-benzyl:



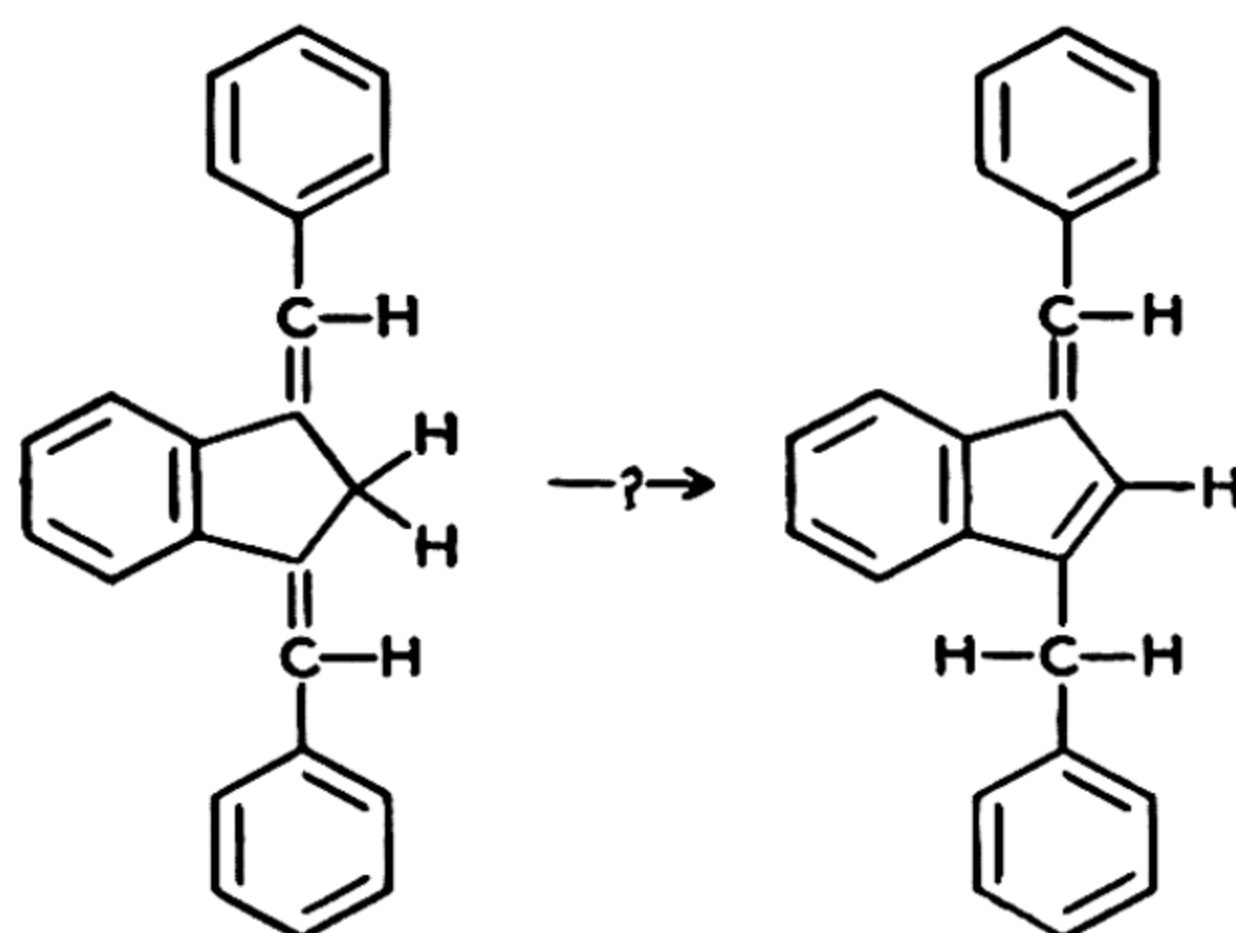
1-Diphenylmethylene-indane, heated with concentrated hydrochloric acid, forms 3-benzhydrylindene.¹²⁶ The shift of the double bond into the adjacent ring is patterned after the isomerization of terpinolene. 1-Benzhydrylindene, when treated with potassium methoxide solution, gives 3-benzhydrylindene also.^{126, 127} The different roles of acid and alkali serve to clarify the course of these reactions:



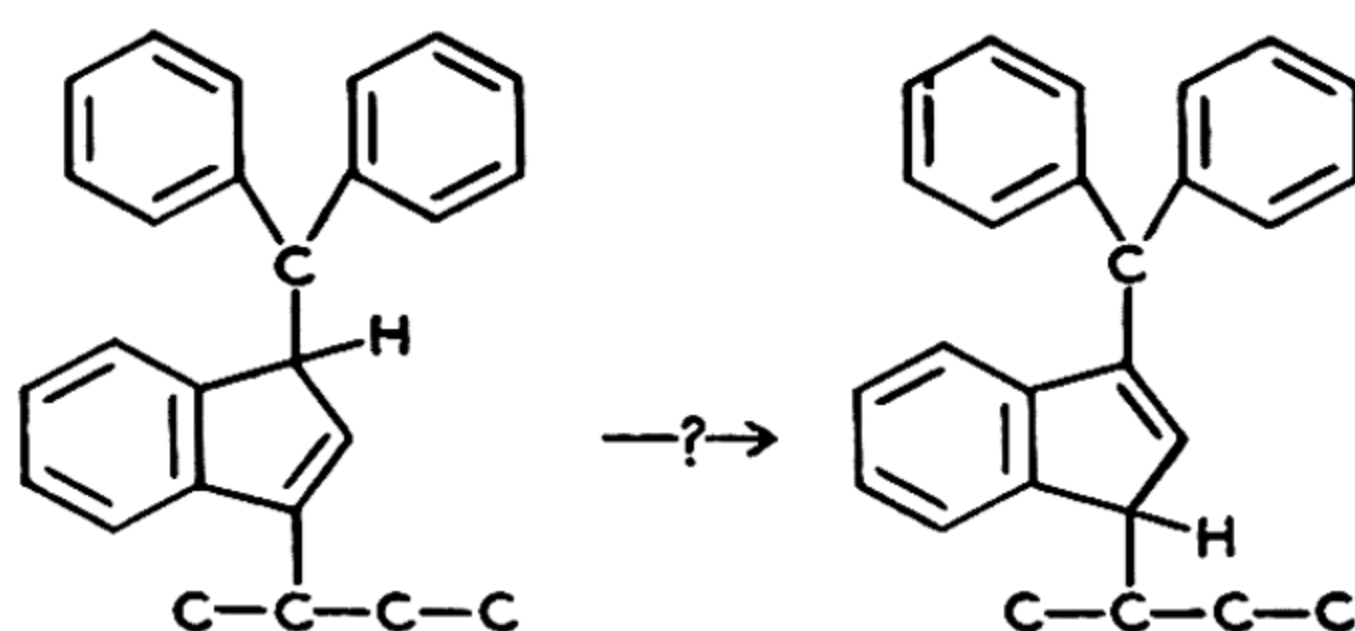
1,2-Diphenylindene, when boiled with alcoholic potash, yields a precipitate of 2,3-diphenylindene.^{69, 428} This isomerization obviously involves only an "allylic" migration of hydrogen:



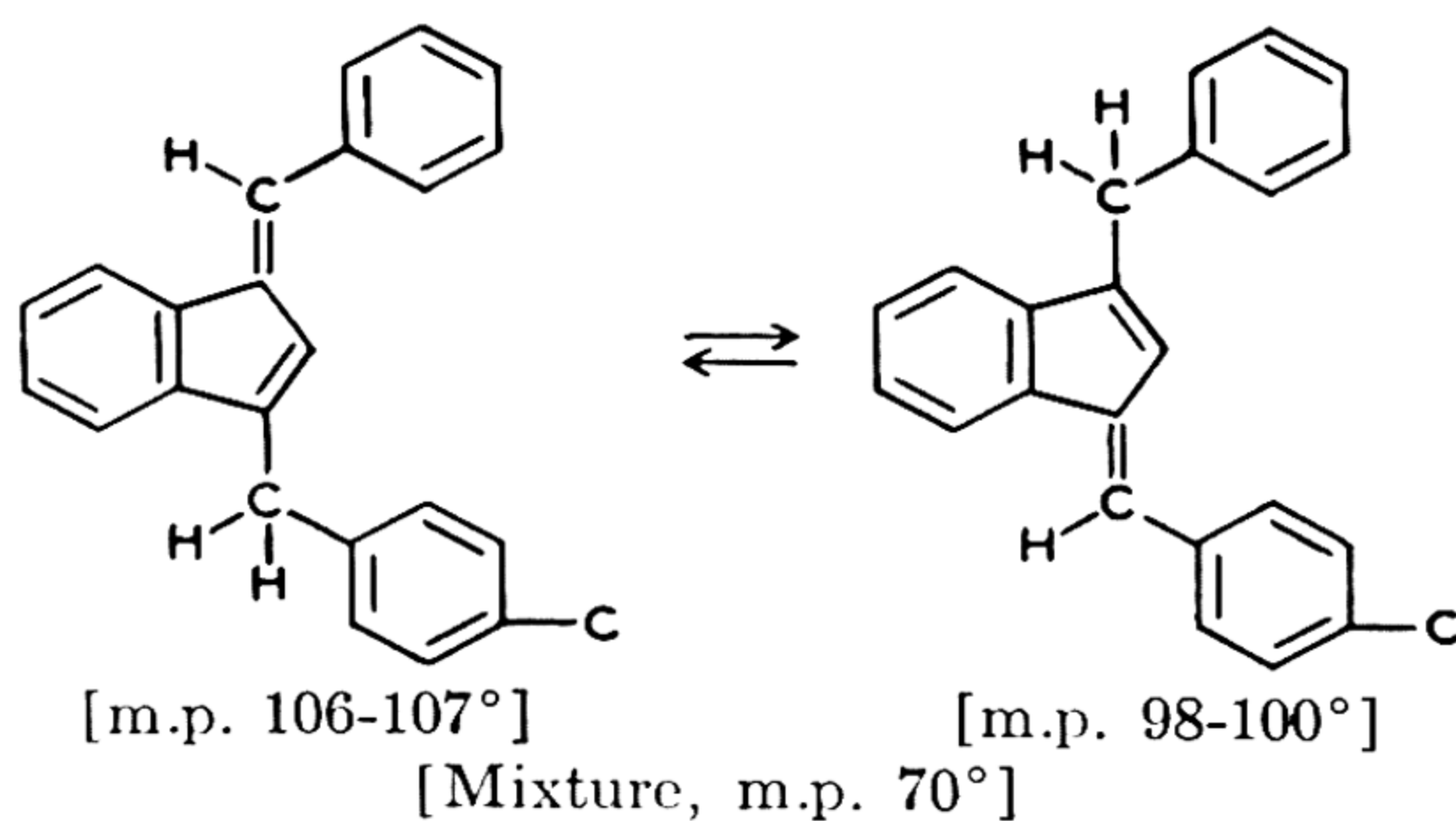
1,3-Dibenzylidene-indane is the structure proposed by the authors for a colorless compound, $C_{23}H_{18}$, of m.p. 213° . The latter underwent a slow change into the yellow 1-benzylidene-3-benzylindene when heated at a temperature over 213° or when subjected to vacuum distillation: ⁵⁷⁹

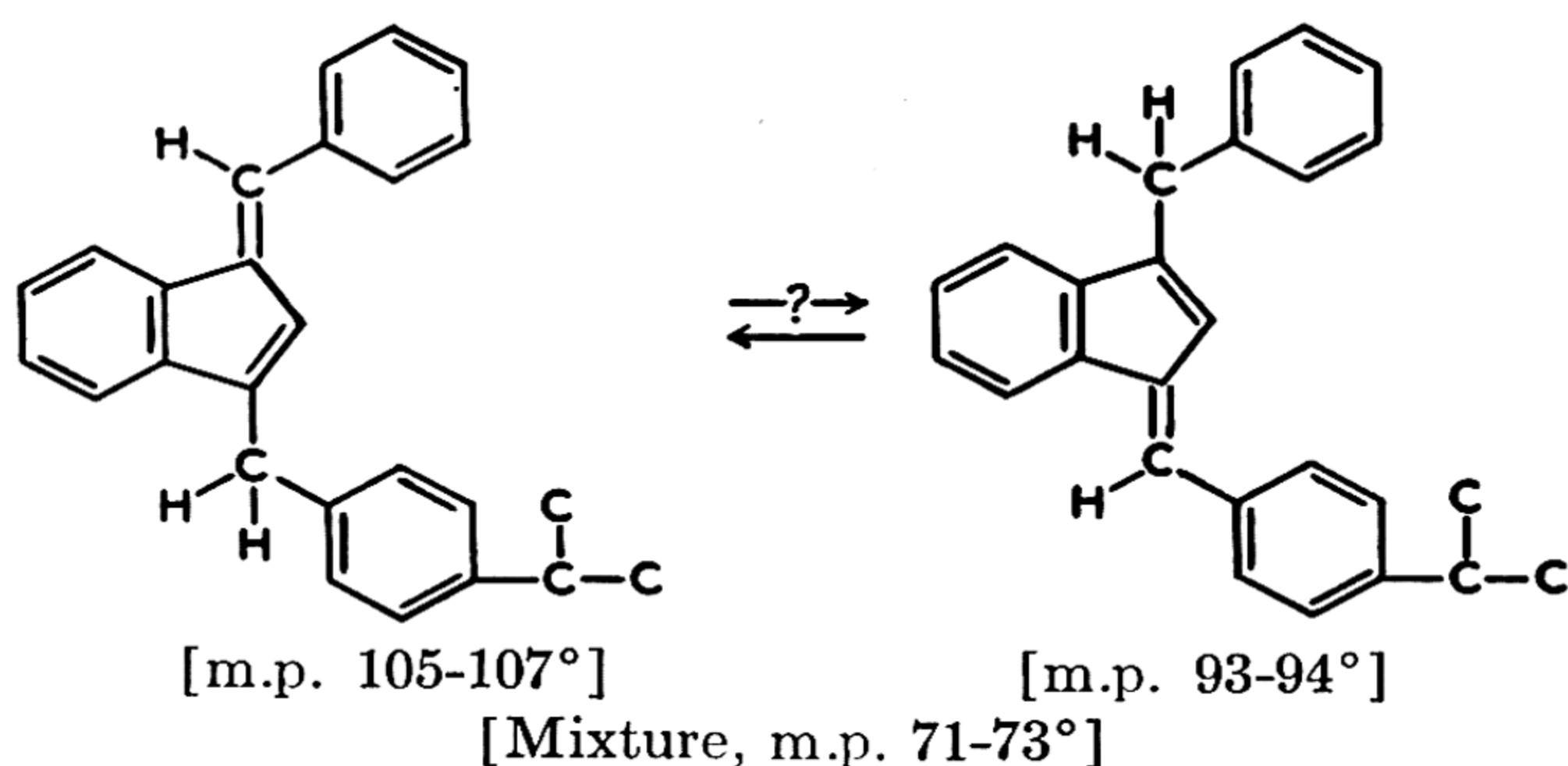


1-Benzhydryl-3-*sec*-butyl-indene, likewise, is the structure proposed by the authors for a colorless compound (m.p. $121-123^\circ$) which, boiled with potassium methoxide solution, gives another colorless isomer (m.p. $94-95^\circ$).⁶⁵⁶ The last isomer is probably 1-*sec*-butyl-3-benzhydrylindene:

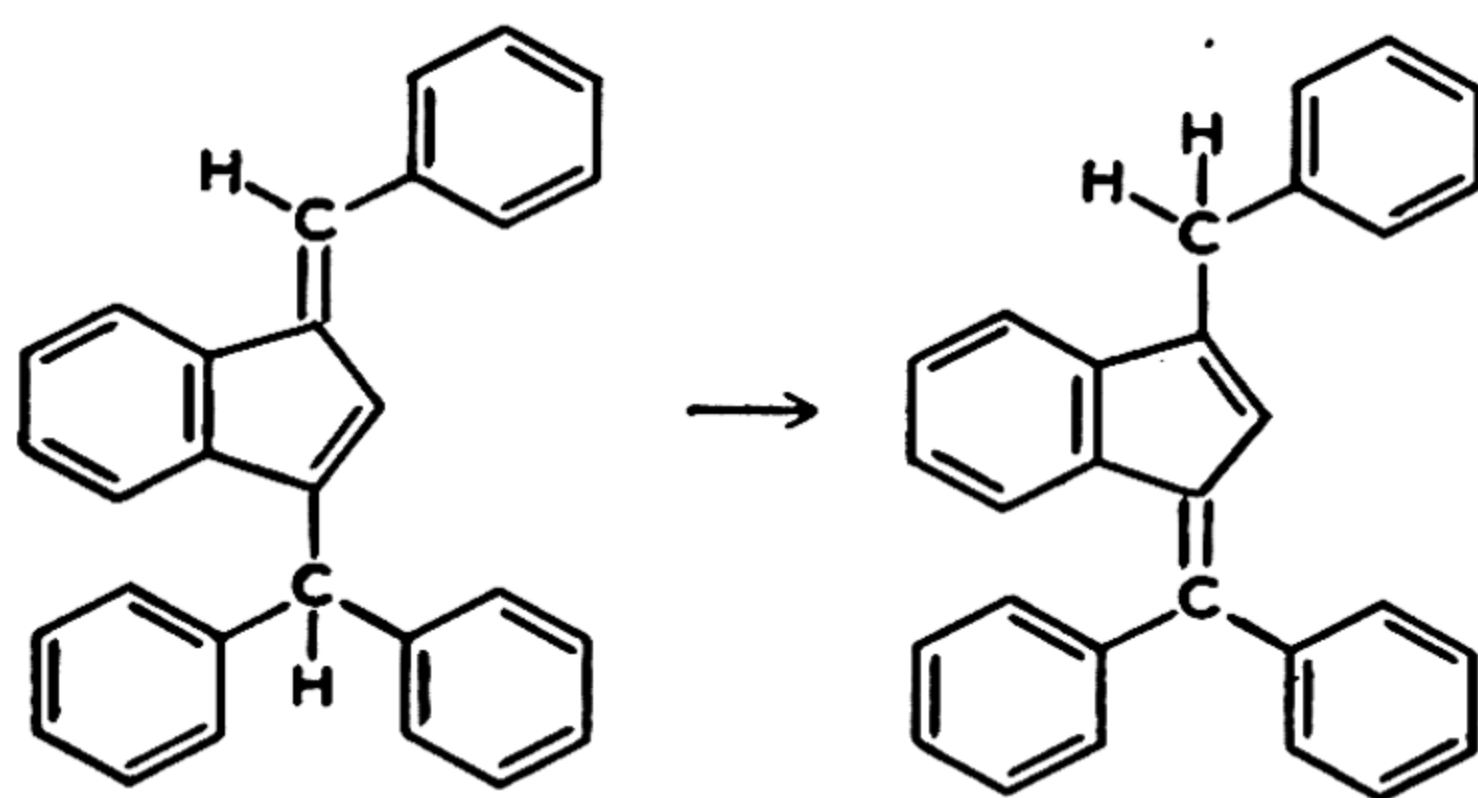


1-Benzylidene-3-*p*-methylbenzyl-indene and 1-*p*-methylbenzylidene-3-benzylindene both form the same equilibrium mixture (m.p. 70°) when boiled with methanolic potash.⁵⁹ 1-*p*-Isopropylbenzylidene-3-benzylindene, when boiled with potassium methoxide solution, also gives an "equilibrium mixture" (m.p. $71-73^\circ$) containing some newly formed 1-benzylidene-3-*p*-isopropylbenzylindene.⁵⁹ These isomerizations are merely an *endo-exo* oscillation of 2 conjugated double bonds under the influence of alkaline media:

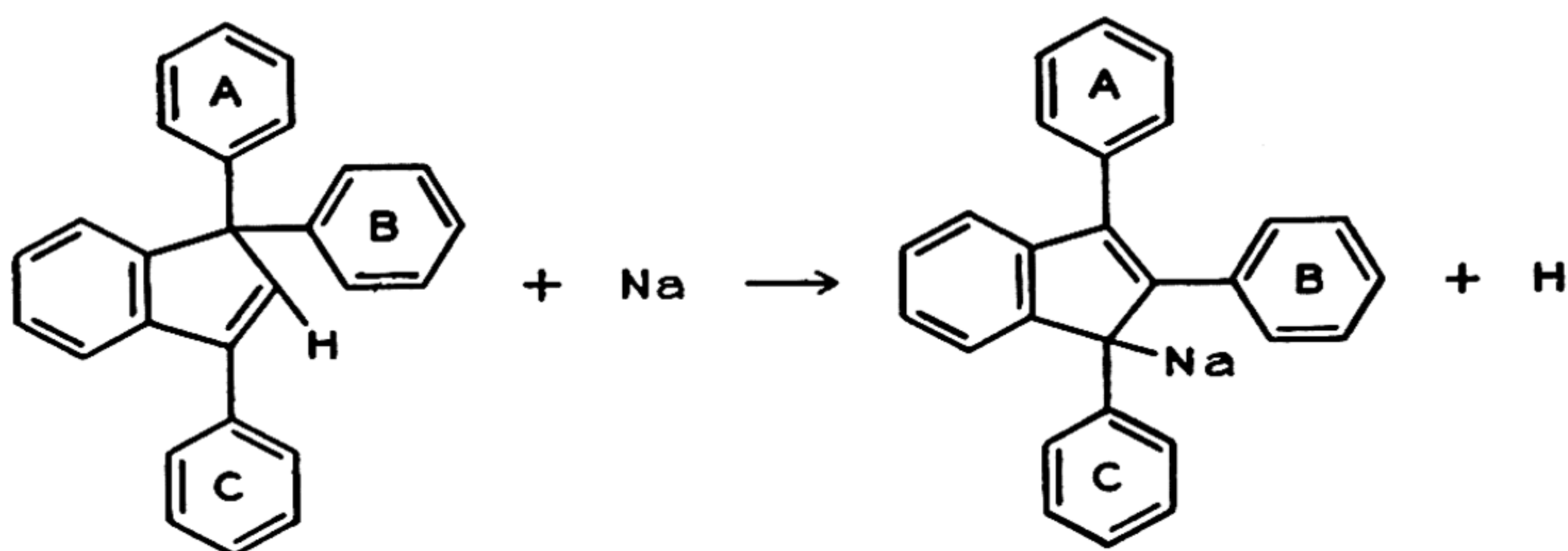




1-Benzylidene-3-benzhydryl-indene, boiled with potassium methoxide solution, formed 1-diphenylmethylene-3-benzylindene: ⁶⁵⁶



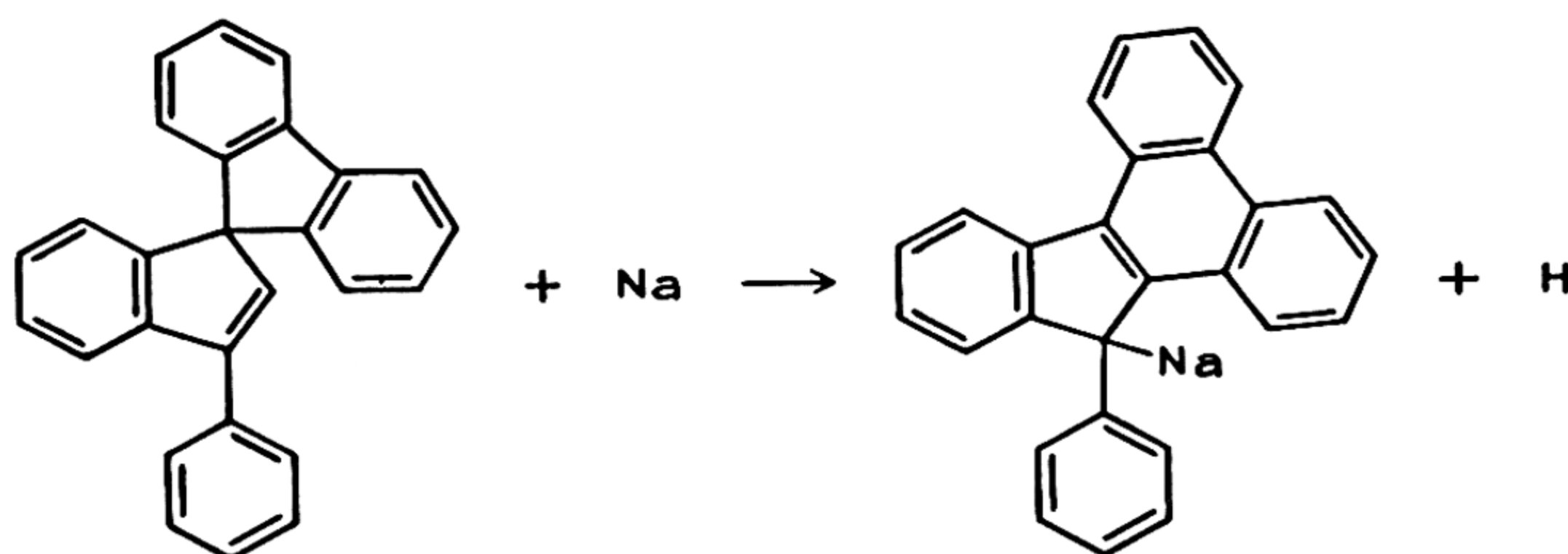
The treatment of 1,1,3-triphenylindene with sodium resulted in the migration of a phenyl group and in the formation of the sodium derivative of 1,2,3-triphenylindene: ⁶⁷⁸



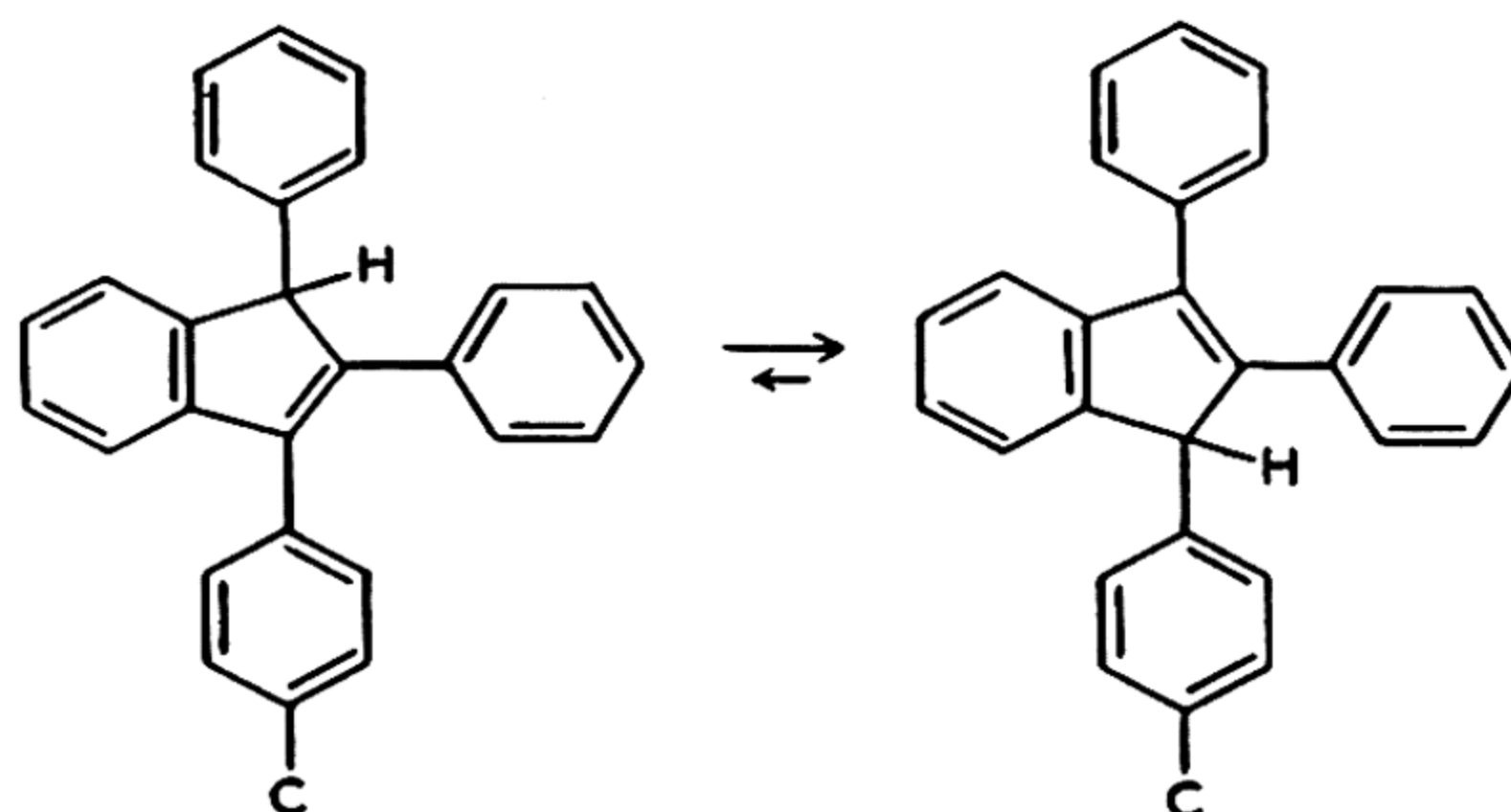
This, and some of the preceding reactions, are more complex than revealed by either their equations or the nomenclature of the hydrocarbons themselves. In view of the known behavior of indenenes as a three-carbon system, it is desirable to write these equations with labeled phenyl groups, which would indicate double bond migrations.

1-Methyl-1,3,3-triphenylindane remained unchanged when heated at 215° for 6 days with "Floridin." ³³² This hydrocarbon ³³² was originally mistaken for 1,1,3,3-tetraphenylcyclobutane, but later investigations ^{54, 522} have rectified this error. It is of interest to compare at this point the less reactive indanes with the indenenes.

1-Biphenylene-3-phenylindene and sodium gave the sodium derivative of 1,2,3,4-dibenzo-9-phenylfluorene.^{313, 314} The sodium derivative, when acted upon by alcohol, forms the free hydrocarbon 1,2,3,4-dibenzo-9-phenylfluorene. The action of an excess of lithium on an ether solution of 1-biphenylene-3-phenylindene for 3 days also gave 1,2,3,4-dibenzo-9-phenylfluorene (80 per cent).³¹⁶ The course of these isomerizations is evident from the following equation:



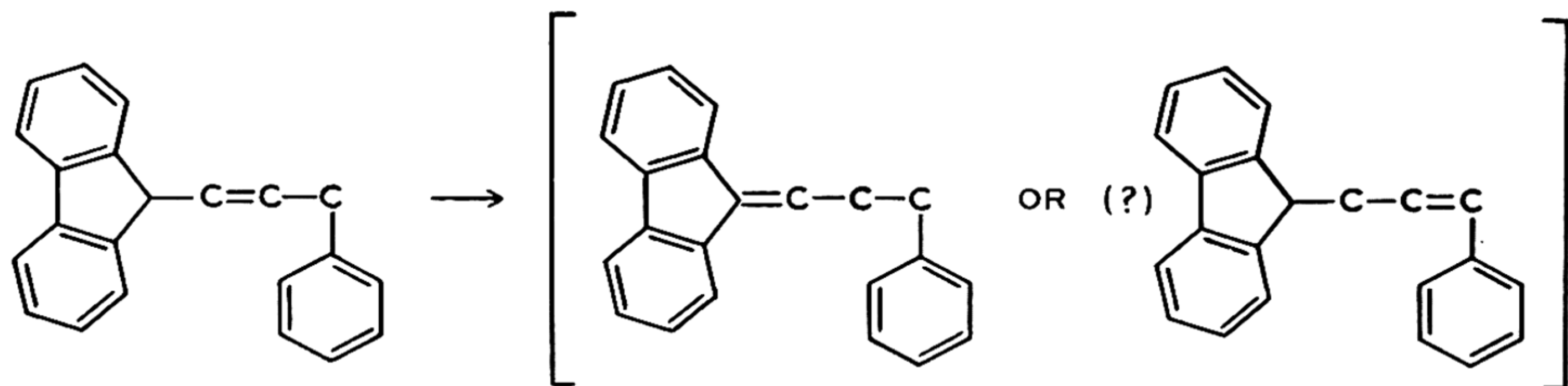
1,2-Diphenyl-3-*p*-tolylindene, boiled 1.25 hours with alcoholic potash, formed an equilibrium mixture of 1-*p*-tolyl-2,3-diphenylindene (90 per cent) and unchanged initial hydrocarbon (10 per cent).³¹⁵ Both 1,2-diphenyl-3-*p*-tolylindene and 1-*p*-tolyl-2,3-diphenylindene reacted with sodium amalgam in the presence of ether, forming sodium derivatives. Hydrolysis of the last compounds brought about the formation of practically the same mixture of indenenes.³¹⁵ From this particular observation, the conclusion was drawn that the anion present is labile and that it is responsible for the occurrence of the equilibrium mixture. Moreover, it was probably correctly pointed out that the replacement of sodium by hydrogen immediately terminates the reaction at the equilibrium point established by the anions :



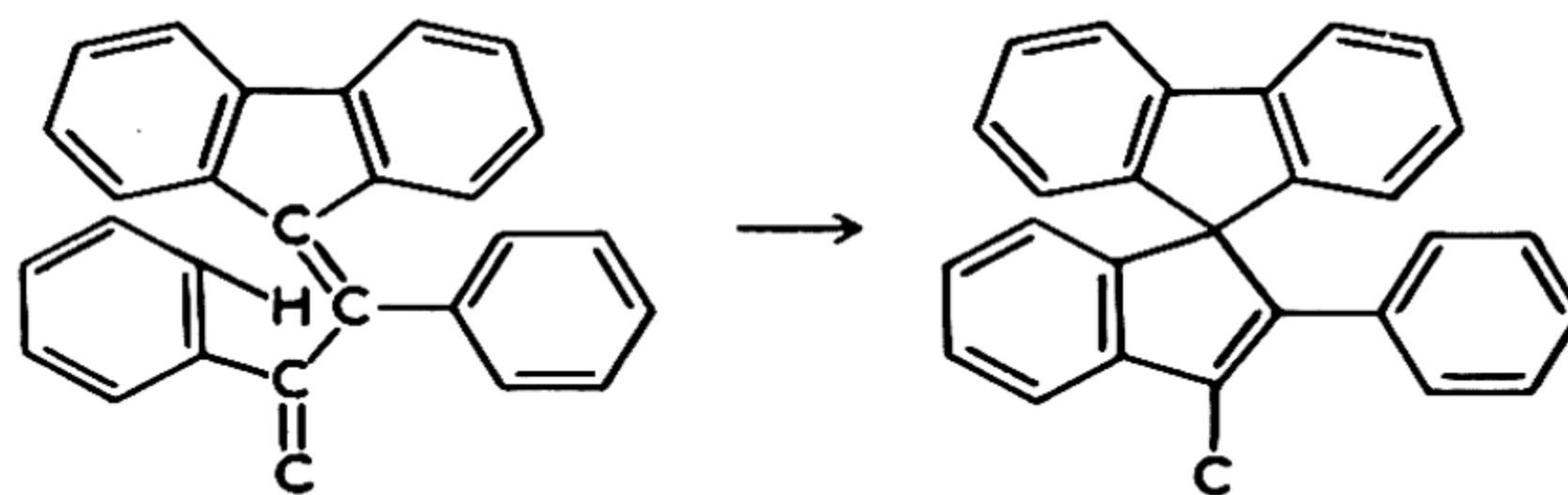
Fluorenes

1-Biphenylene-4-phenylbutene-2 (*i.e.*, “ Δ^2 - dihydrocinnamylidene-fluorene”), when heated under reflux for 2 hours with sodium ethoxide solution, or when boiled for a long time with alcoholic piperidine, formed an isomer (m.p. 81-82°).⁵⁸⁰ The new isomer was considered to be either

1-biphenylene-4-phenylbutene-1 (*i.e.*, “ Δ^1 -dihydrocinnamylidene-fluorene”) or “possibly” 1-phenyl-4-biphenylenebutene-1 (*i.e.*, “ Δ^3 -dihydrocinnamylidenefluorene”):



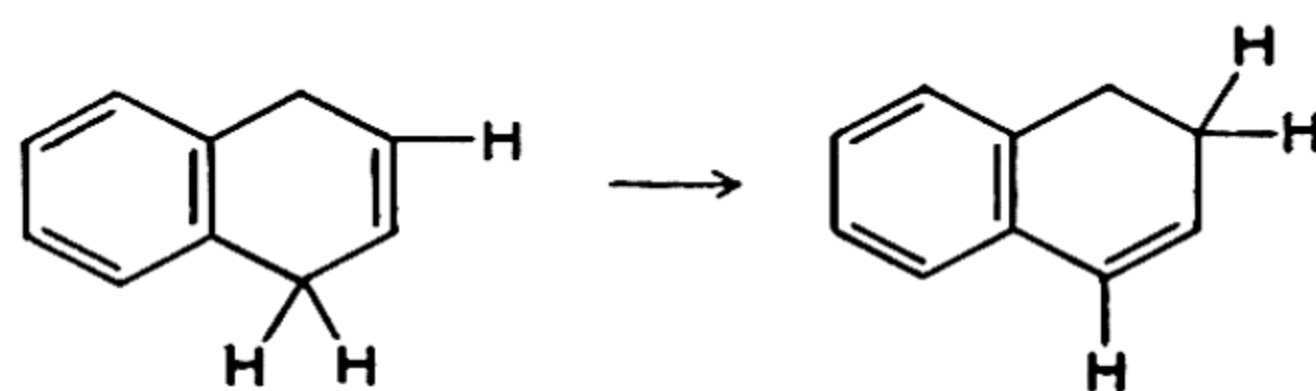
1-Biphenylene-2,3-diphenylbutadiene-1,3 was isomerized to 1-biphenylene-2-phenyl-3-methylindene (75 per cent) when boiled for an hour with acetic acid containing a small quantity of sulfuric acid.^{316a} This cyclization involves an interesting 1:4 addition of a labile hydrogen atom from an ortho position:



Naphthalenes

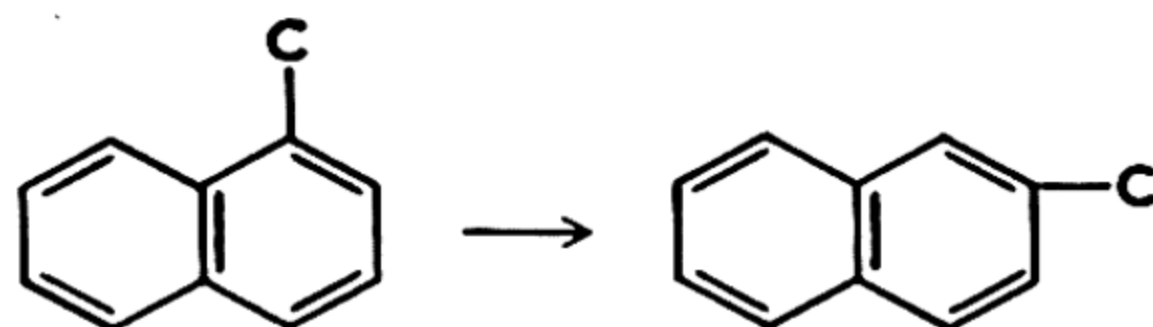
It is known that naphthalenes have a predisposition to change from 1-substituted into 2-substituted derivatives,⁴⁷⁸ and that the latter are preferentially formed in the Friedel-Crafts reactions.

1,4-Dihydronaphthalene was isomerized to 1,2-dihydronaphthalene on heating at 100-105°⁵⁷³ or at 150°⁵³⁰ with a 10-per cent sodium ethoxide solution, or with a 5-per cent solution at 140-150°.⁵⁷⁴ These isomerizations are in conformity with the substitution rule for naphthalenes, in spite of the presence of a cyclohexadiene ring, since a hydrogen atom migrates from 4-position into 2-position. The formation of 1,2-dihydronaphthalene corresponds to an allylic-type of isomerization:

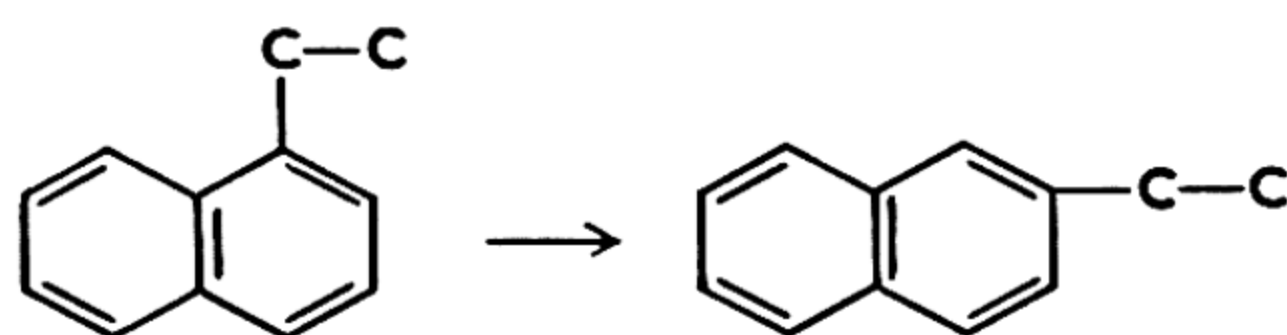


1,2-Dihydronaphthalene is 4.9 kilocalories per gram-mole more stable than 1,4-dihydronaphthalene.^{184a, 575aa}

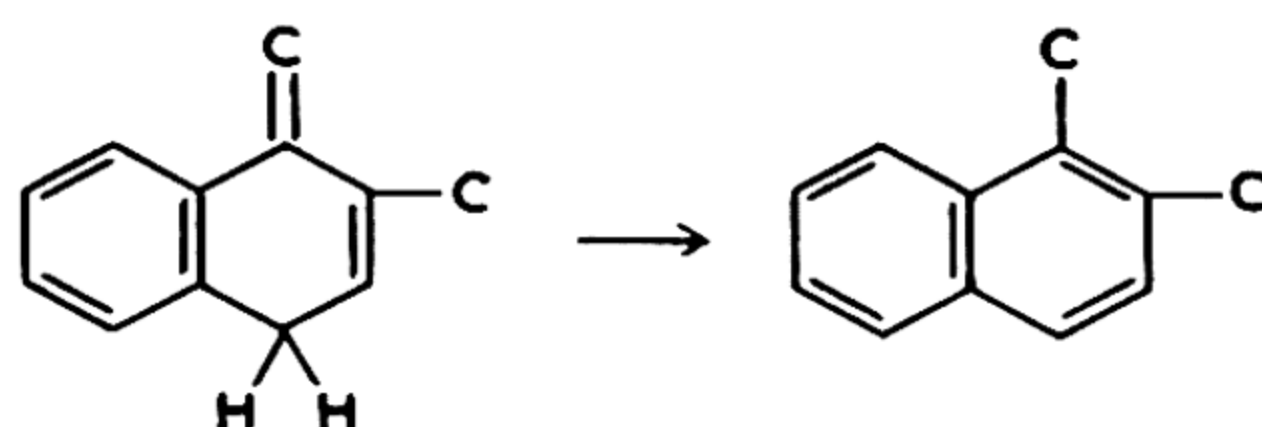
1-Methylnaphthalene, passed over silica gel at 420° in the presence of nitrogen, gave about 39 per cent of 2-methylnaphthalene: ³⁶⁵



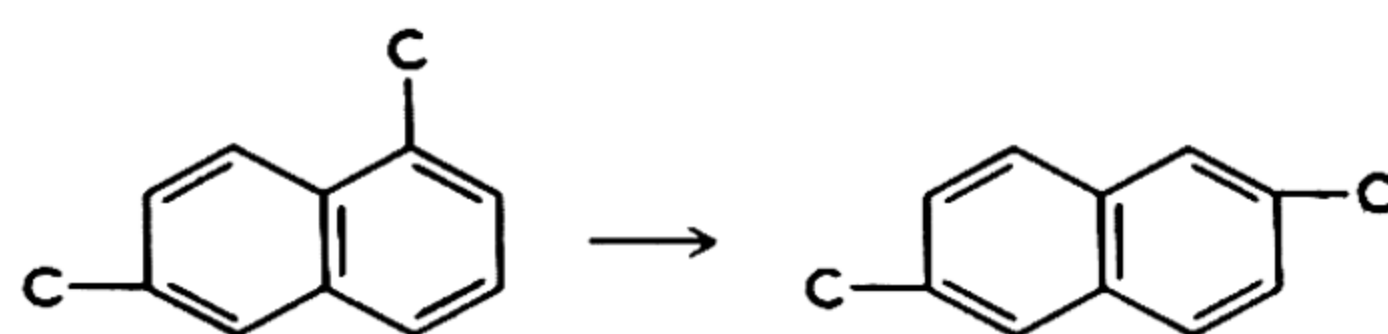
1-Ethylnaphthalene at $420-430^{\circ}$ gave similarly 2-ethylnaphthalene: ³⁶⁵



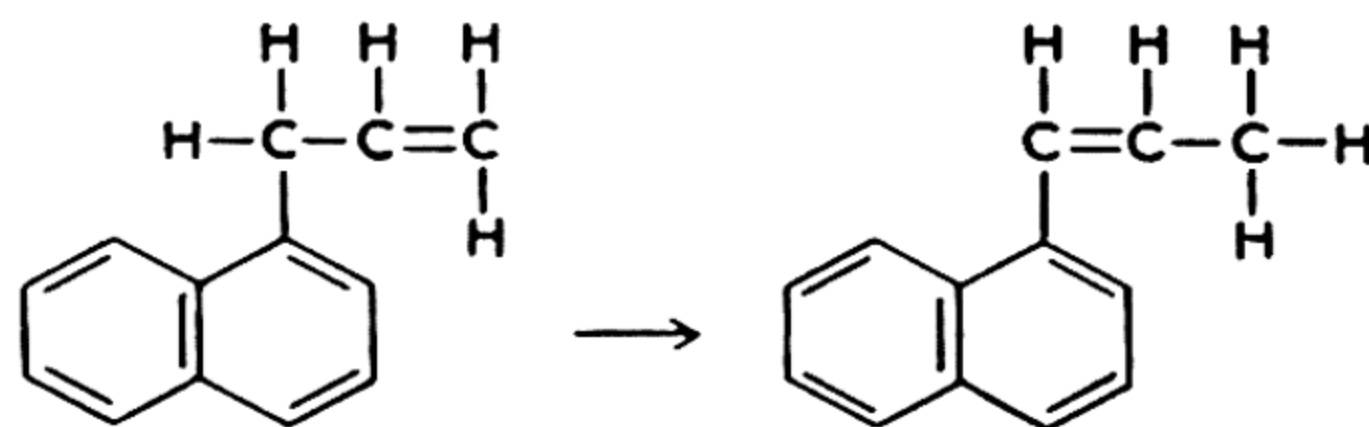
1-Methylene-2-methyl-1,4-dihydronaphthalene undergoes aromatization to 1,2-dimethylnaphthalene when boiled with acetic acid plus hydrogen chloride.⁵²⁹ This reaction exemplifies a shift of a double bond into a ring under the influence of an acidic catalyst. Two double bonds move into new positions, as would be expected in the case of a five-carbon or "double allylic" system:



1,6-Dimethylnaphthalene when passed over silica gel at $400-420^{\circ}$ gave 20 per cent of 2,6-dimethylnaphthalene and a considerable amount of the unchanged hydrocarbon: ³⁶⁵

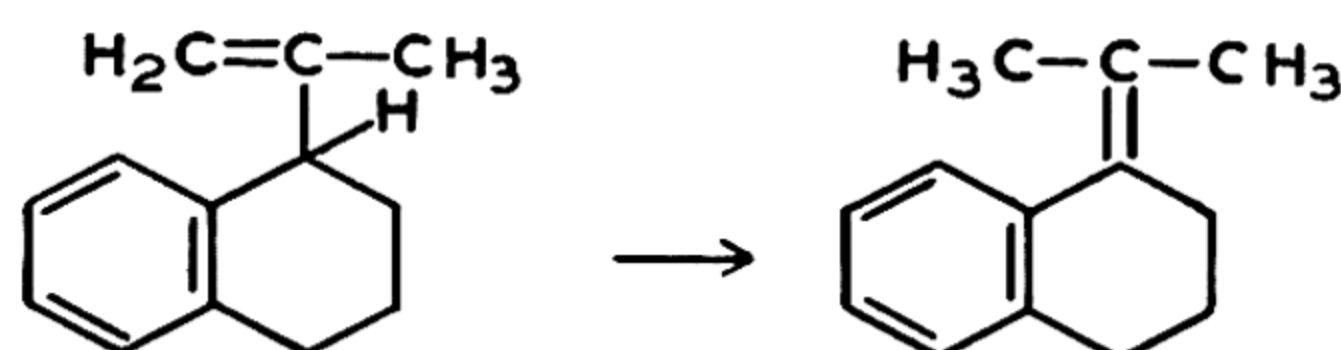


Passage of 1-allylnaphthalene through a tube filled with activated alumina at $500-550^{\circ}$ and a pressure of 15 mm. Hg caused isomerization to 1-propenylnaphthalene.¹⁸⁵ A temperature of 300° is adequate for a slow isomerization over alumina.^{342a} Boiling alcoholic potash effects the same reaction: ⁵⁸⁵



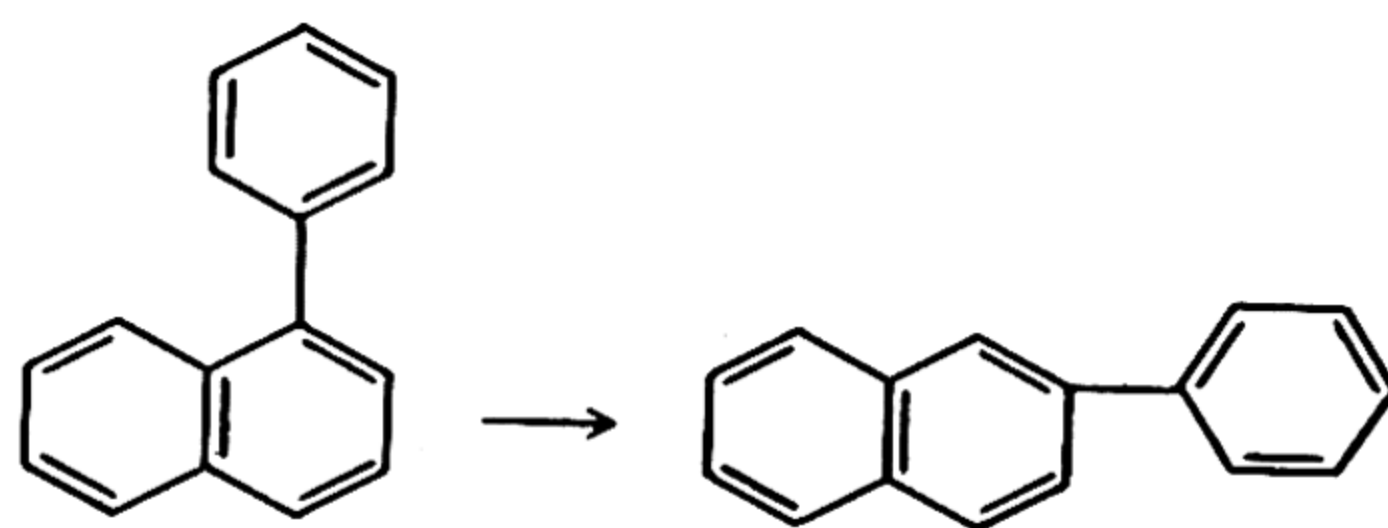
1-Isopropenyl-1,2,3,4-tetrahydronaphthalene isomerizes to at least 75 per cent of 1-isopropylidene-1,2,3,4-tetrahydronaphthalene upon being

heated with sodium ethoxide solution.²⁹⁹ This high yield is to be expected on account of the alkaline catalyst, which causes an arrest of the double bond at the ring position:

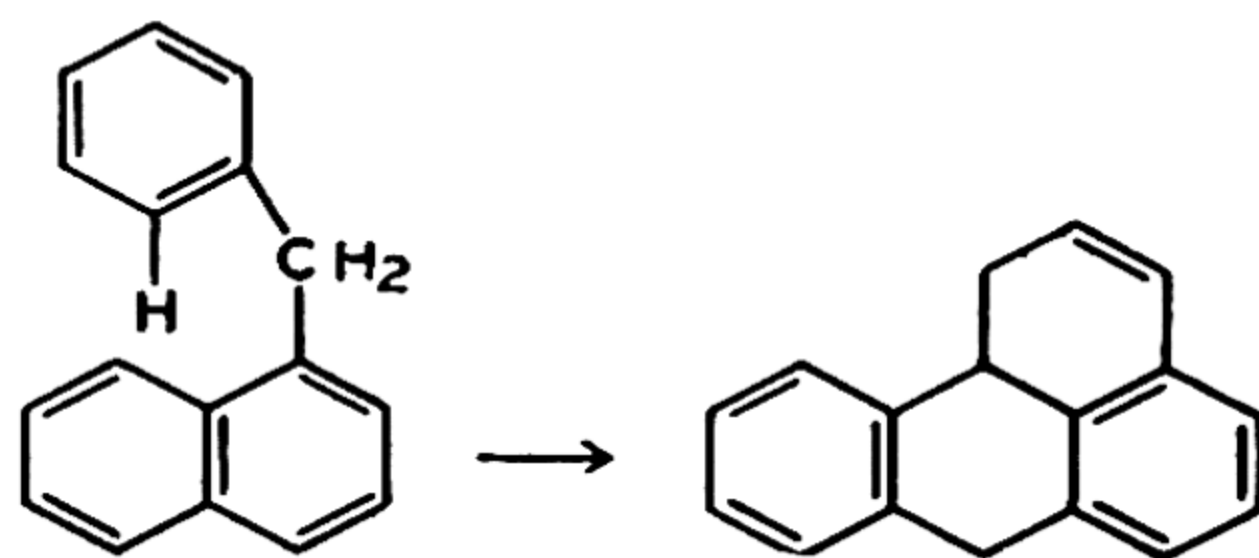


The reaction is related to the limonene-terpinolene isomerization, having the same type of hydrogen migration.

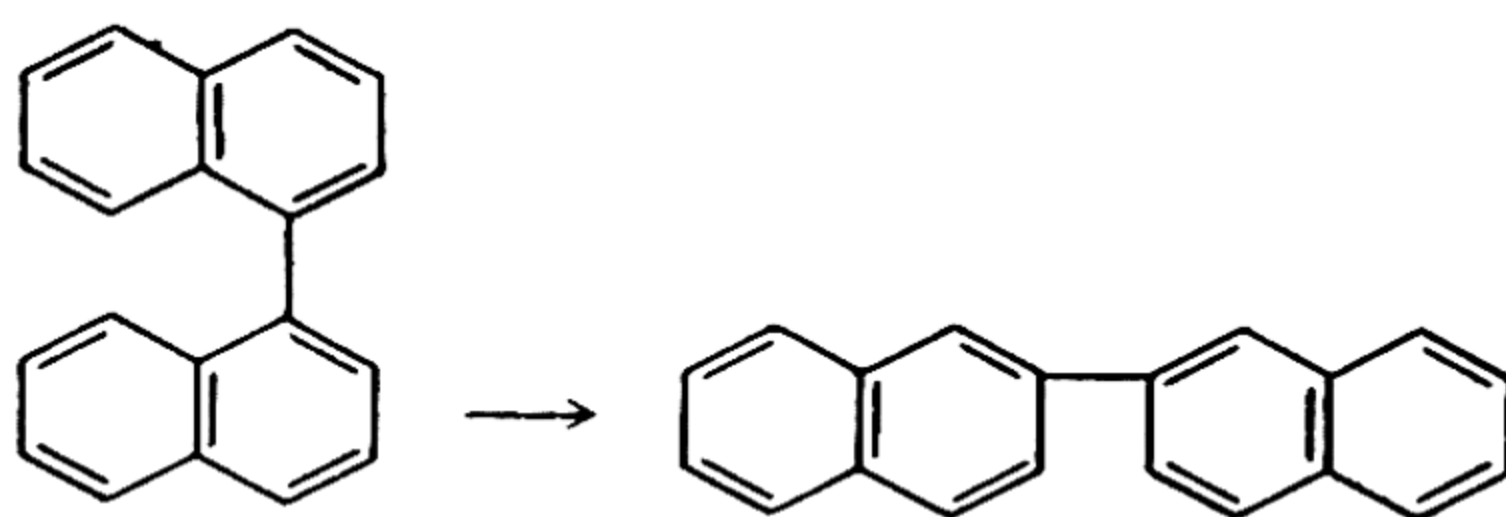
1-Phenylnaphthalene was isomerized to 2-phenylnaphthalene at 350° in the presence of silica gel, cobalt silicate, and copper silicate as catalysts, using either air or hydrogen as the vapor carrier:³⁶⁵



1-Benzyl-naphthalene isomerized to 1,11b-dihydro-7-benz[de]-anthrene upon passage through an empty "glowing" tube,²²⁵ or through one containing pumice.⁵²⁵ The product at first was assumed to be C₁₇H₁₂ or "isochrysofluorene."²²⁵ Later work,⁵²⁵ determined its true composition, C₁₇H₁₄, which corresponds to a "dihydrobenzanthrene." The reaction can be considered as an intramolecular alkylation requiring the closure of phenyl and hydrogen upon an active double bond within the naphthalene ring:

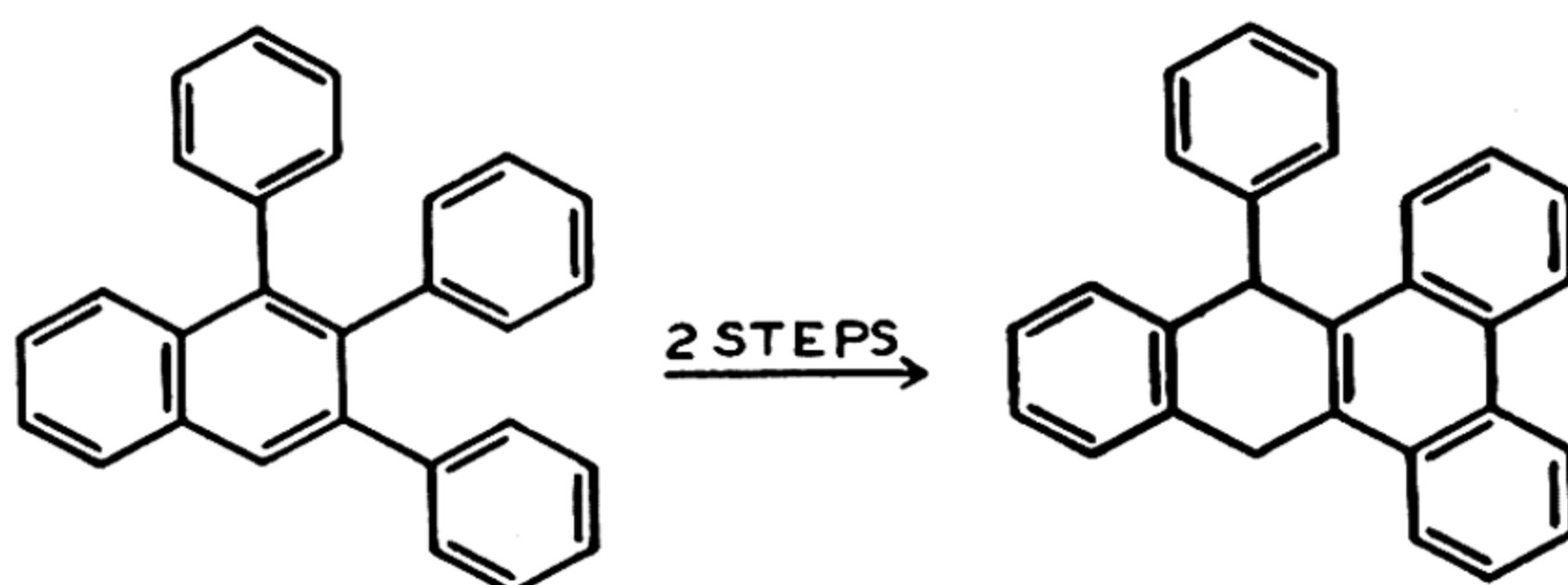


1,1'-Dinaphthyl, heated with aluminum chloride in the presence of carbon disulfide, forms some 2,2'-dinaphthyl:⁵²⁶



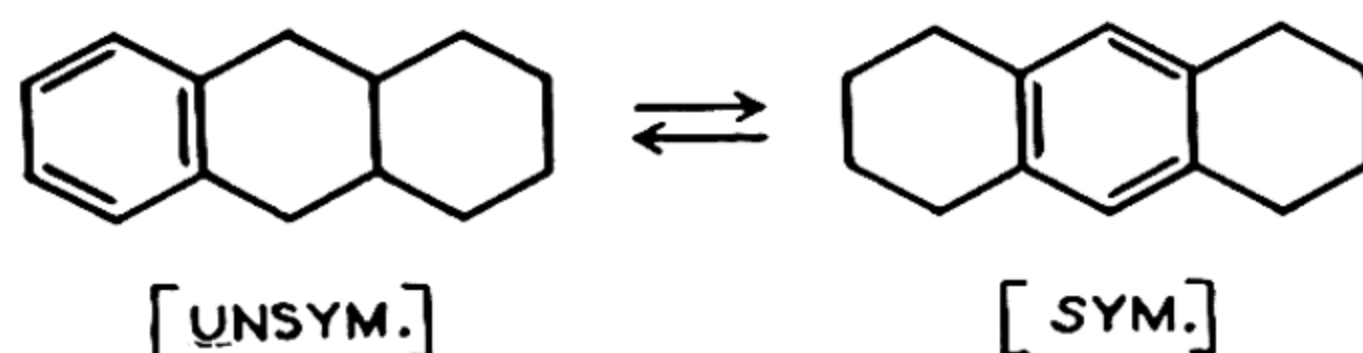
This isomerization is similar to that of 1-phenylnaphthalene.

1,2,3-Triphenylnaphthalene, agitated with lithium for 8 days in ether solution, yielded a colored precipitate. The latter formed 9-phenyl-9,14-dihydro-dibenz[ac]anthracene (*i.e.*, 9-phenyl-9,10-dihydro-1,2,3,4-dibenzanthracene) upon contact with alcohol: ^{57a}

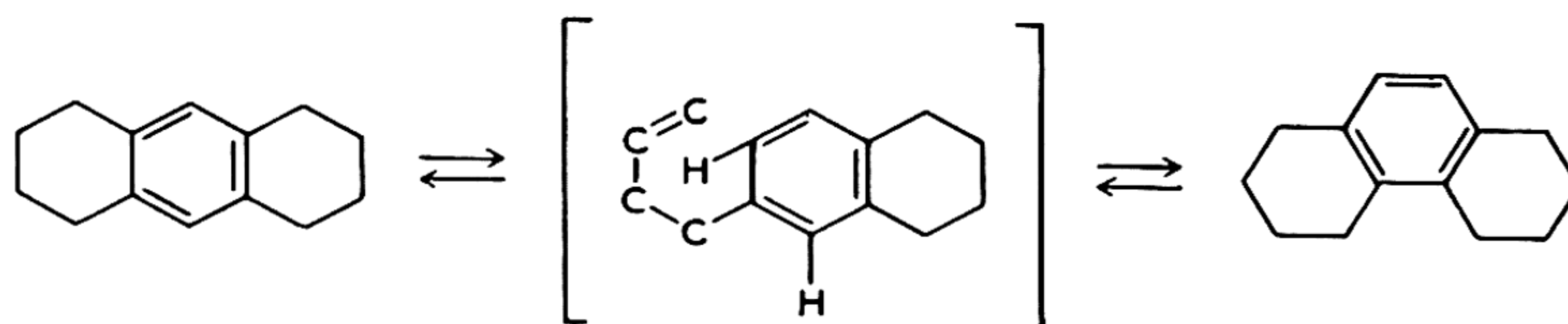


Anthracenes

1,2,3,4,4a,9,9a,10- and 1,2,3,4,5,6,7,8-Octahydroanthracenes undergo an interconversion, or extensive dehydrogenation plus hydrogenation, when heated at 340-370° and 335°, respectively, for several hours at 100 atmospheres' hydrogen pressure with molybdenum disulfide as catalyst.⁴⁵⁰ Since yields were not reported, it is impossible to state which isomer is the more stable. The interconversion of these unsymmetrical and symmetrical octahydroanthracenes indicates that at least two of the three double bonds within an aromatic ring can shift into an attached fused-ring:

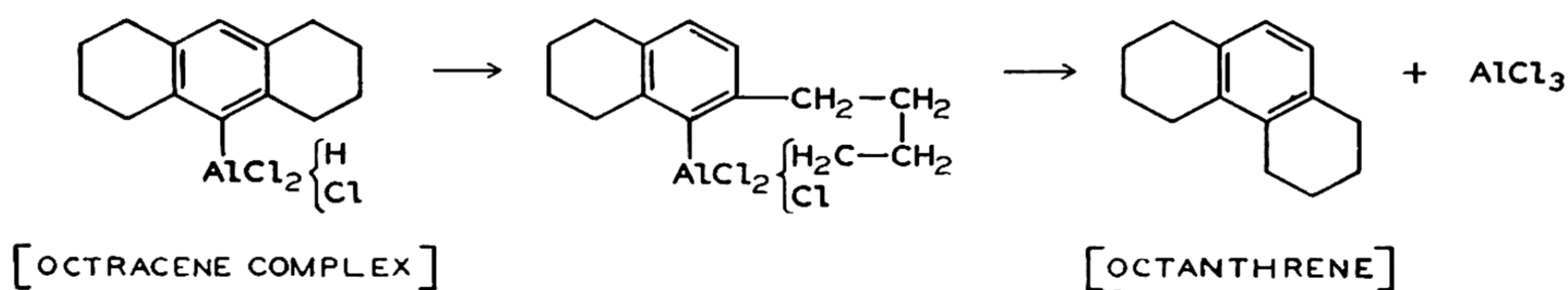


However, 1,2,3,4,5,6,7,8-octahydroanthracene, when treated similarly with molybdenum disulfide at the higher temperature point of 390°, yielded 34.25 per cent of 1,2,3,4,5,6,7,8-octahydrophenanthrene.⁴⁵³ The presence of the last product can be explained by assuming (a) the formation of 1,2,3,4-tetrahydro-6-(3-butenyl)naphthalene as an intermediate and (b) the acquisition of a labile hydrogen at the phenanthrene "6" position by removal from the anthracene "10" position. This would be an example of a simple dealkylation plus alkylation in a condensed ring system:

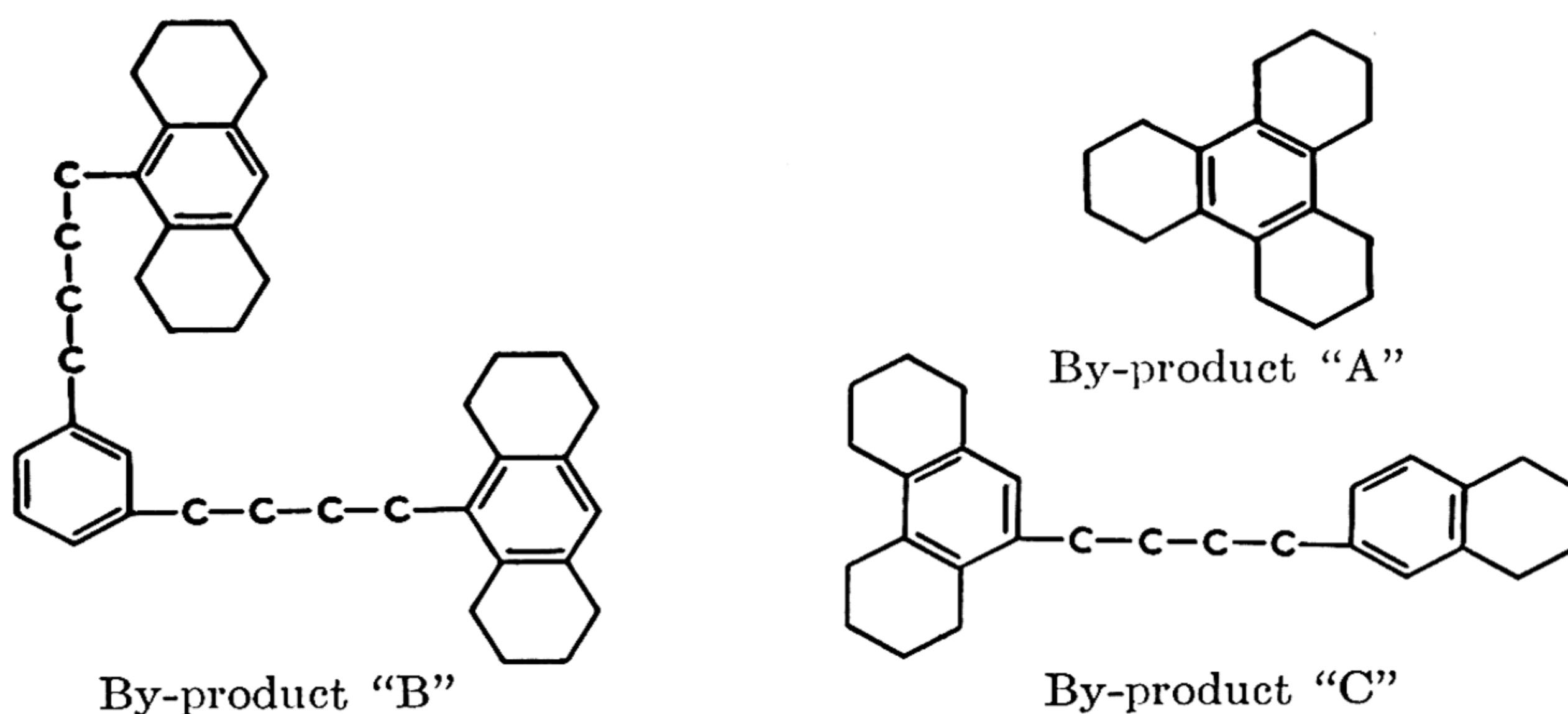


In the next section, under "Phenanthrenes," it is shown that this isomerization is reversible when aluminum chloride is used as catalyst. 1,2,3,4,5,6,7,8-Octahydroanthracene, heated with aluminum chloride at 70-80°,

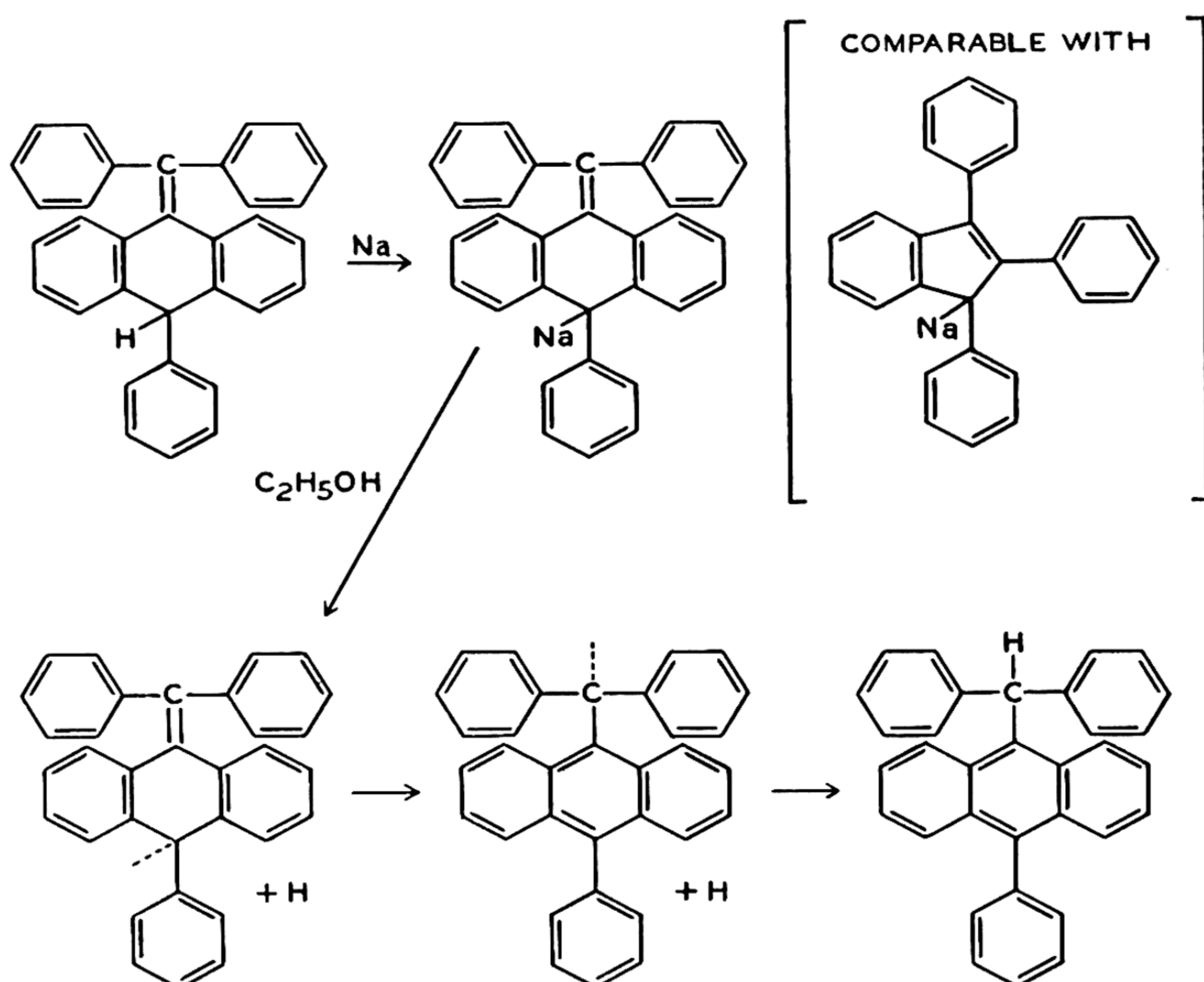
yielded 40-44 per cent of 1,2,3,4,5,6,7,8-octahydrophenanthrene (*i.e.*, octanthrene), together with 44 per cent of the starting hydrocarbon, 4.4-4.8 per cent of dodecahydrotriphenylene (*i.e.*, "A"), 4.0 per cent of a combined fraction of "phenylene-bis-octracenylobutane" [this may be "B," *i.e.*, 1,3-bis-(4-[9-octracenyl]-butyl)benzene] and "tetralyl-octanthrenyl-butane" [which may be "C," *i.e.*, 6-(4-[9-octanthrenyl]butyl)-1,2,3,4-tetrahydronaphthalene], and a small amount of a yellow hydrocarbon (m.p. 320°).⁵²⁸ This reaction was interpreted by assuming the preliminary formation of an octracenyl-aluminum chloride-hydrochloride:⁵²⁸



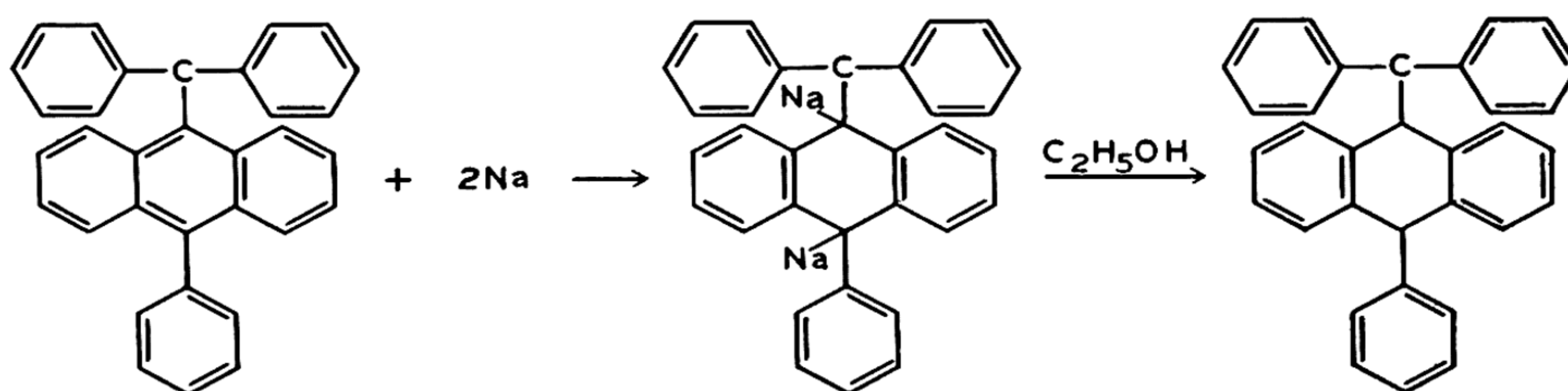
The by-products "A," "B," and "C," are in support of this assumption:



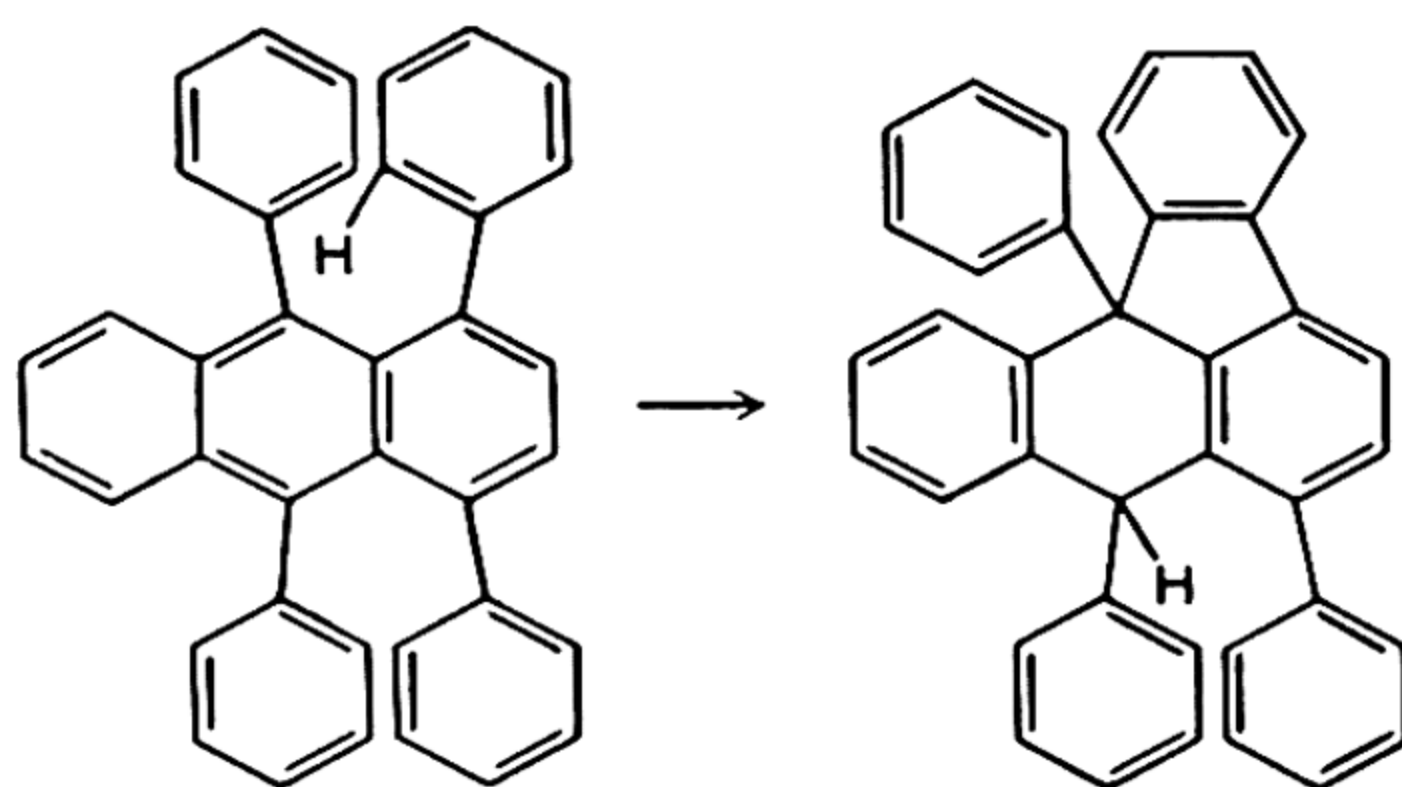
9-Benzohydrylidene-10-phenyl-9,10-dihydroanthracene, agitated with sodium for 8 days in ether solution, gave a dark-red coloration, due to formation of a monosodium substitution product. Treatment of the scarlet-red precipitate of the organosodium product (obtainable after 10 weeks of shaking in the presence of sodium), with alcohol, led to the formation of 9-benzohydryl-10-phenylanthracene.⁴⁴ The structure of the monosodium derivative of 9-benzohydrylidene-10-phenyl-9,10-dihydroanthracene was considered by the experimenter to be analogous to that of the sodium derivative of 1,2,3-triphenylindene. Hydrolysis probably led to the formation of the corresponding free radical, which then isomerized to another free radical related directly to 9-benzohydryl-10-phenylanthracene:



The foregoing metalation plus demetalation is irreversible. 9-Benzohydryl-10-phenylanthracene gave a blue-violet coloration when agitated with sodium powder for 8 days in ether solution, due to the formation of a disodium addition product.⁴⁴ Treatment of the resulting solution with alcohol, and thereafter with water, gave 9-benzohydryl-10-phenyl-9,10-dihydroanthracene:

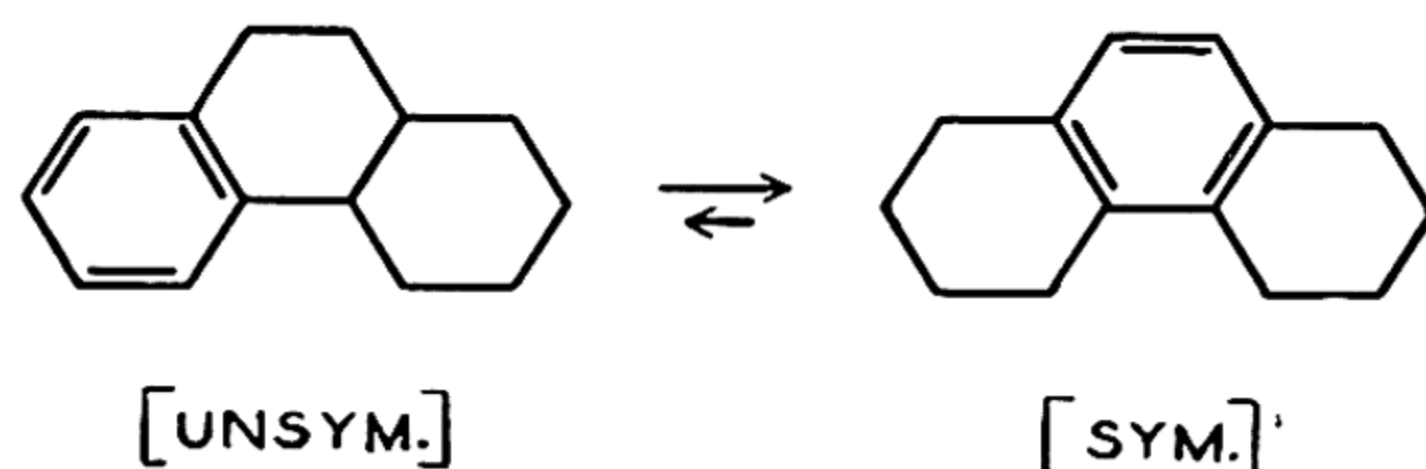


1,4,9,10-Tetraphenylanthracene, when heated under reflux with an excess of formic acid, formed 4,9,10-triphenyl-1,9-(*o*-phenylene)-9,10-dihydroanthracene: ⁶⁴⁰

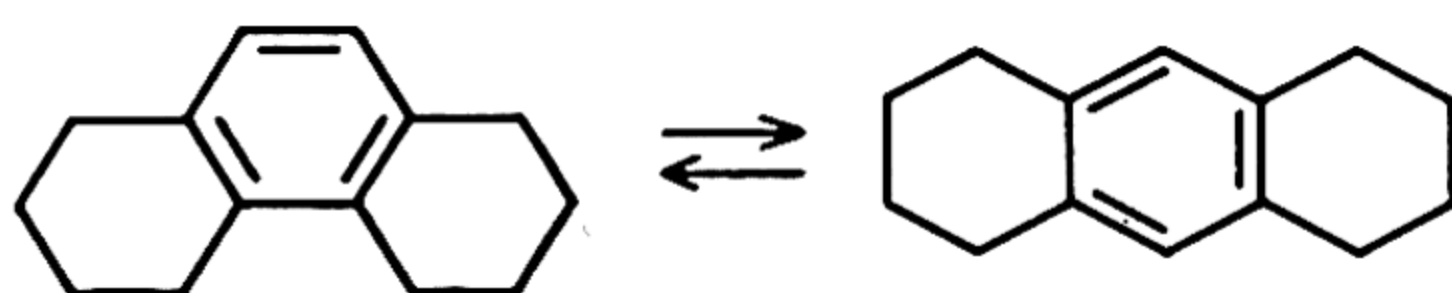


Phenanthrenes

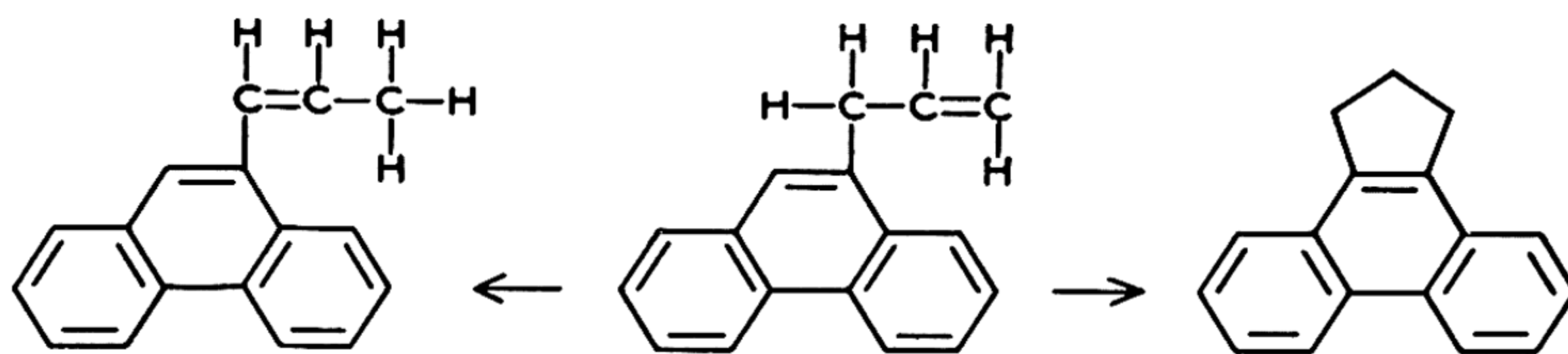
1,2,3,4,4a,9,10,10a- and 1,2,3,4,5,6,7,8-Octahydrophenanthrenes (5-31 g.) undergo an interconversion, or dehydrogenation plus hydrogenation, when heated at 130° for 2-10 hours in a steel bomb at 100-140 atmospheres' pressure of nitrogen with Raney's nickel (2-3 g.), or at temperatures 50-100° higher with copper-chromium oxide (2-4 g.).¹⁵⁰ Since only 3-4 per cent of unsym-octahydrophenanthrene formed, the symmetrical octahydrophenanthrene is the more stable isomer. The former gave at least 15 per cent of the latter after 5 hours of treatment, and 28 per cent after 19 hours. The interconversion of these isomers confirms the observation that at least two of the three double bonds within an aromatic ring can shift into an attached fused-ring:



1,2,3,4,5,6,7,8-Octahydrophenanthrene (*i.e.*, octanthrene) can undergo also an isomerization into 1,2,3,4,5,6,7,8-octahydroanthracene (*i.e.*, octracene). Heated with aluminum chloride at 80°, the former gave a mixture of octanthrene and octracene (45 per cent of each), together with dodecahydrotriphenylene (10 per cent) and other hydrocarbons: ⁵²⁸

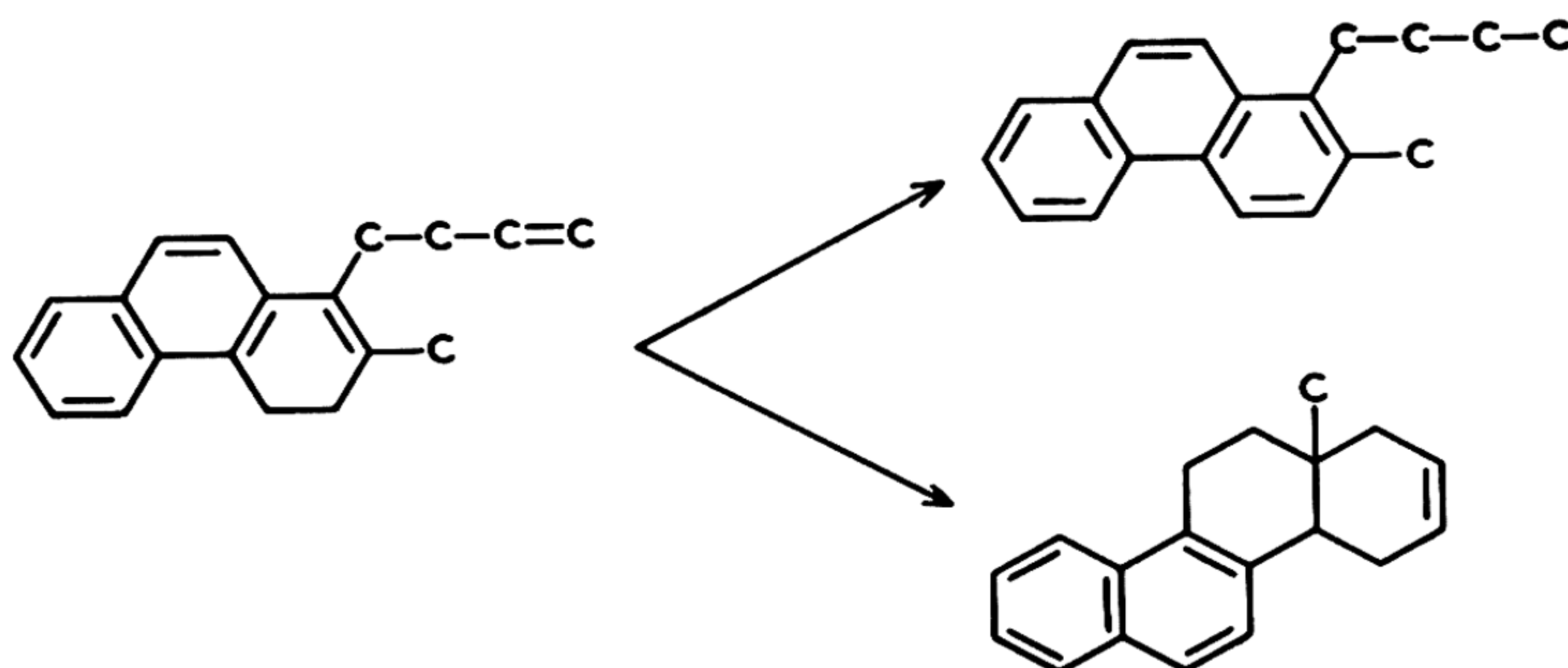


9-Allylphenanthrene isomerized to 9-propenylphenanthrene upon boiling with alcoholic potash for 4 hours,⁴⁷ but gave 2,3-dihydro-1-cyclopenta[*l*]phenanthrene (*i.e.*, 9,10-cyclopentenophenanthrene) when treated with excess of lithium (in ether), then with alcohol to hydrolyze a mono-substitution product (lithium at the α -position on allyl), and thereafter separated from some regenerated 9-allylphenanthrene: ⁵⁸



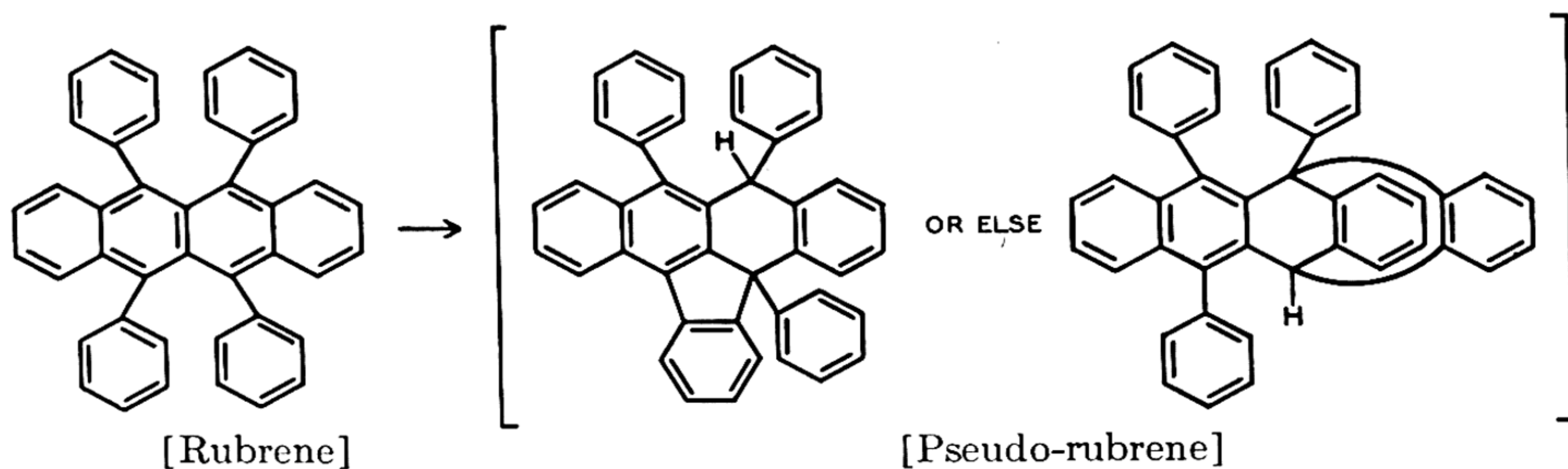
1-(3-Butenyl)-2-methyl-3,4-dihydrophenanthrene yielded 1-butyl-2-methylphenanthrene when heated successively at 260-265° and 280-285°

with palladinized charcoal.^{95a} Treatments with phosphorus pentoxide at 140° or 170°, or else with acetic acid plus phosphoric acid at 100°, led to the formation of a methylhexahydrochrysene, presumably 12a-methyl-1,4,4a,11,12,12a-hexahydrochrysene: ^{95a}



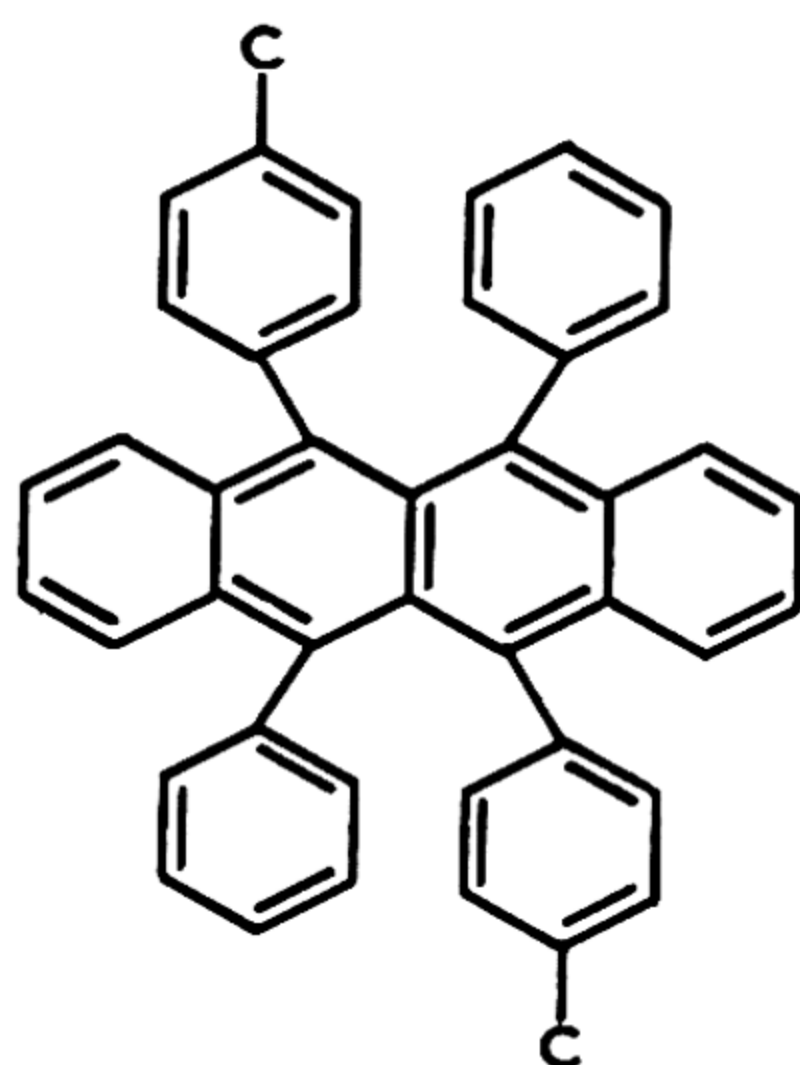
Naphthacenes

The action of gaseous hydrogen iodide upon solutions of 5,6,11,12-tetraphenylnaphthacene (*i.e.*, rubrene) yielded an isomer (pseudo-rubrene) and reduction products.^{34, 143, 387, 388} Two structures have been proposed for pseudo-rubrene.¹⁴² One of the proposed structures, that of 5,11,12-triphenyl-5,6-(*o*-phenylene) - 5,12 - dihydronaphthacene, seems preferable to the other: ⁶⁴⁰



Reduction of rubrene by gaseous hydrogen iodide dissolved in ether gives two colorless "dihydorubrenes" (m.p. 230-231° and 249-250°). The higher-melting compound is capable of isomerization into the lower-melting product when heated with sodium isoamylate solution.¹⁴³ These "dihydorubrenes" seem to be quite different from the yellow isomers (C₄₂H₃₀) via isomerization of 1,3,3,4,4,6-hexaphenylhexadiyne-1,5, encountered in the section of "Alkynyl Benzenes." Hence, the colorless "dihydorubrenes" can be considered as dihydronaphthacenes, more or less "phenylenated."

Treatment of a benzene solution of dimethylrubrene with a strong acid, such as sulfuric acid, gave two isomers that are difficult to separate and which have melting points of 271-272° and 293-294°, respectively.¹⁶⁵



Probable Structure of Dimethylrubrene

Isomerizations of the condensed aromatics are listed systematically in Table 40,* p. 384.

Conclusions

1. Indanes with unsaturated side-chains isomerize into indenenes under thermal conditions or in the presence of acidic catalysts.

2. Isomerizations observed in the group of simpler indenenes include: (a) an allylic type of hydrogen migration, (b) redistributions of aryl groups, (c) cyclizations, and (d) *endo-exo* oscillation of two conjugated double bonds.

3. Fluorene derivatives undergo changes in unsaturated side-chains. One fluorene isomerizes in the manner of butene-2 into butene-1. Another fluorene, with a side-chain containing two double bonds and phenyl groups, undergoes a cyclization to an indene with a biphenylene side-chain.

4. Isomerizations of naphthalenes include: (a) several allylic types of hydrogen migration in ring and side-chain, (b) redistributions of alkyl and aryl groups, (c) cyclizations, and (d) "aromatization."

5. Anthracenes isomerize by hydrogen migration. The latter caused: (a) the cyclization of an "unhydrogenated" polyaryl anthracene, (b) decyclization plus cyclization within an octahydrogenated anthracene, with development of a new ring system, and (c) the stabilization of liquid "perhydrogenated" anthracene by the formation of a solid form. This series of isomerizations indicates a relationship between cyclization and the degree of unsaturation of these molecules.

6. Phenanthrenes isomerize by: (a) hydrogen migration within ring and side-chain or from ring to side-chain (aromatization), (b) cyclization, and (c) decyclization plus recyclization.

* This table lacks a few examples given in Tables 41 and 42.

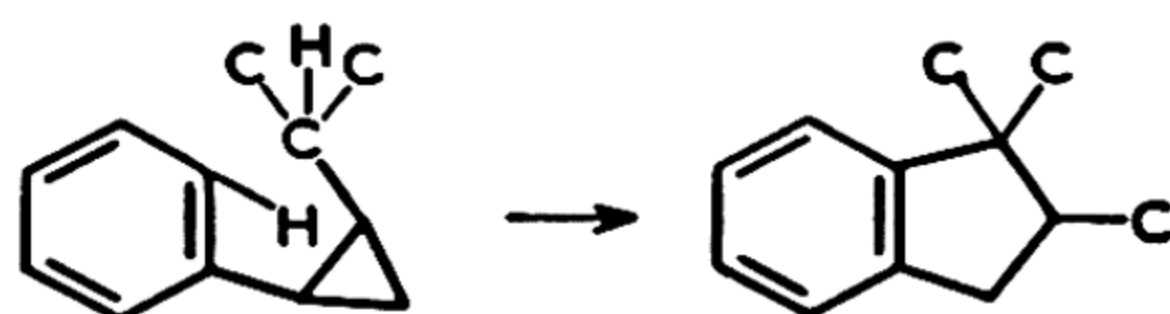
7. Rubrenes and hydrorubrenes, which are highly condensed aromatics or naphthacenes, probably isomerize by cyclization involving *o*-phenylenation.

AROMATIC-CYCLANE HYDROCARBONS

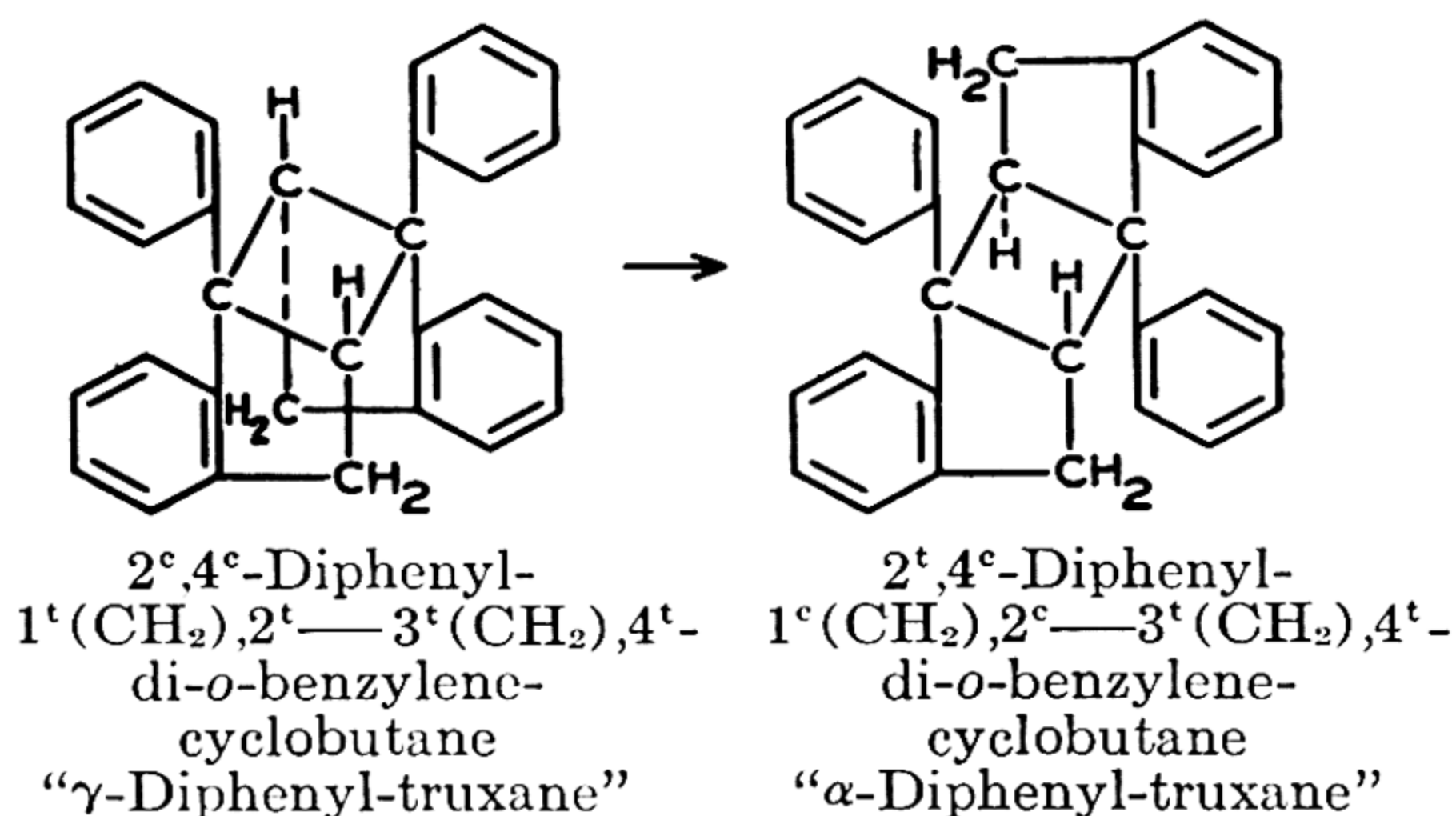
Only a few examples of isomerization are known in the group of cyclanes containing phenyl groups. This is indicative partly of the stable structures usually assigned to cyclanes and to the benzene ring. These isomerizations are considered in order of increasing size of the cyclane ring.

Isomerizations

1-Isopropyl-2-phenylcyclopropane, treated with 90-per cent sulfuric acid, selectively opens up the cyclopropane ring at one point and forms 1,1,2-trimethylindane.^{131a} This isomerization involves the transfer of two hydrogen atoms:

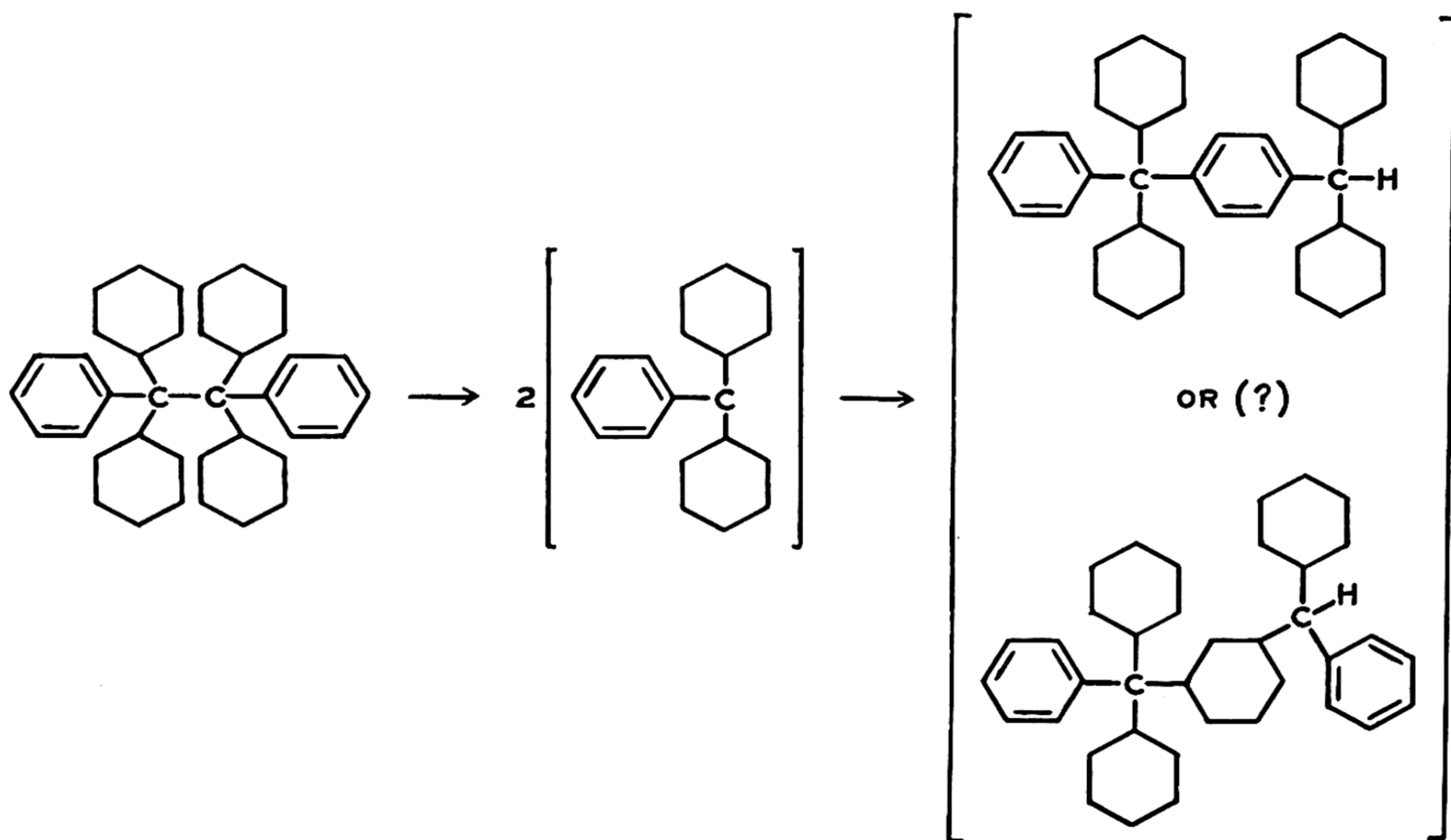


" γ -Diphenyl-truxane," which may be considered both as a "condensed 1,3-dialkyl-2,2,4,4-tetraaryl-cyclobutane" and as a *cis*-diphenyl-*cis*-di-*o*-benzylene-cyclobutane, was isomerized completely when heated at a temperature somewhat above its melting point for 5 hours.⁵⁶⁸ The product of isomerization is " α -diphenyl-truxane," *i.e.*, the corresponding *trans*-diphenyl-*trans*-di-*o*-benzylene-cyclobutane:



1,2,4-Triphenylcyclopentane exists in a metastable liquid form that changes very slowly into a stable solid, which probably is a geometrical isomer.⁴⁰³ 1-Methyl-2,3,5-triphenylcyclopentane and 1,3-dimethyl-2,4,5-triphenylcyclopentane occur likewise in liquid and solid modifications. The liquid forms of these hydrocarbons are the less stable and hence change into stable solid stereoisomers upon aging.¹

1,2-Diphenyl-tetra-cyclohexylethane, dissolved in xylene and heated to 100° for 10 minutes, formed an isomer (m.p. 209°).⁴⁷⁴ The structure of this isomer product was considered to be related to that of *p*-benzohydryl-tetraphenylmethane (the product of isomerization of hexaphenylethane). (*p*-[Di-cyclohexylmethyl] - phenyl) (phenyl) (di - cyclohexyl) - methane and, less likely, (*m*-[phenylcyclohexylmethyl]-cyclohexyl) (phenyl) (di-cyclohexyl)methane are, therefore, hydrocarbons that may comprise the product from 1,2-diphenyl-tetra-cyclohexylethane. The first possible derivative involves the combination of an ordinary trisubstituted methyl free radical with one of its specific aryl-resonance forms; the second or less likely derivative requires the addition of the same trisubstituted methyl free radical to a hypothetical, substituted cyclohexyl free radical:



Treatment of 1,2-diphenyl-tetra-cyclohexylethane (dissolved in ether) with 40-per cent sodium amalgam, followed by carbon dioxide, gave 15 per cent of an isomer (m.p. 209°) and a certain amount of phenyl-di-cyclohexylacetic acid.⁴⁷⁴

The data on isomerizations of aromatic-cyclane hydrocarbons are given in Table 41, p. 390.

Conclusions

Aromatic-cyclane hydrocarbons isomerize to more stable structures upon aging, thermal treatment, or catalytic influence. Catalysts other than sulfuric acid or sodium amalgam to accelerate these interesting isomerizations remain to be found.

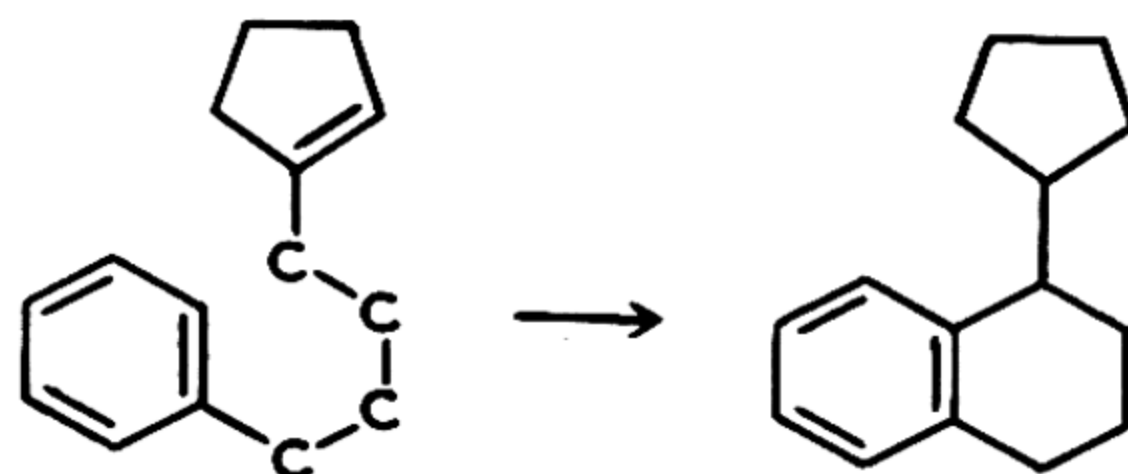
AROMATIC-CYCLENE HYDROCARBONS

Cyclization of an aromatic-cyclene hydrocarbon occurs readily when the cyclene ring is attached univalently to the aromatic. In this reaction the ring closure upon the active double bond can be considered as an intramolecular alkylation with migration of hydrogen. The ease with which cyclization occurs in different directions makes it imperative that experimenters prove the structures and purity of both the unsaturated (reactive) and cyclized hydrocarbons concerned in these isomerizations. Some principles of ring closure governing these cyclizations have been considered in the literature.¹⁶⁰ Generally, the structures of only a few members command the attention of an experimenter. Vast researches are being conducted on carcinogenic and related hydrocarbons, a program which tends to revise their names and some structures.

Isomerizations

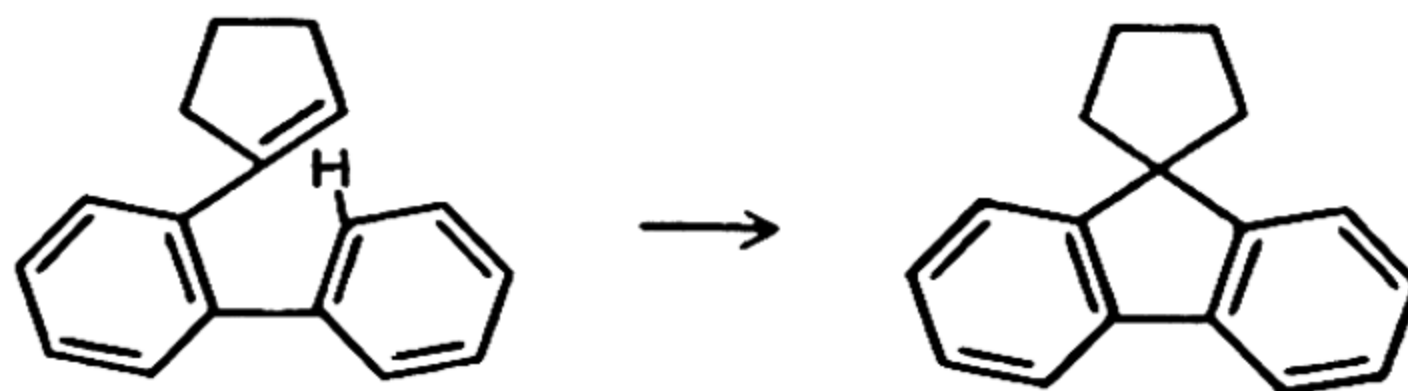
The following 37 related cyclizations are given in order of increasing size of the cyclene rings and side-chains.

1-(4-Phenylbutyl)cyclopentene-1, upon contact with cold sulfuric acid, formed 1-cyclopentyl-1,2,3,4-tetrahydronaphthalene:^{134a}



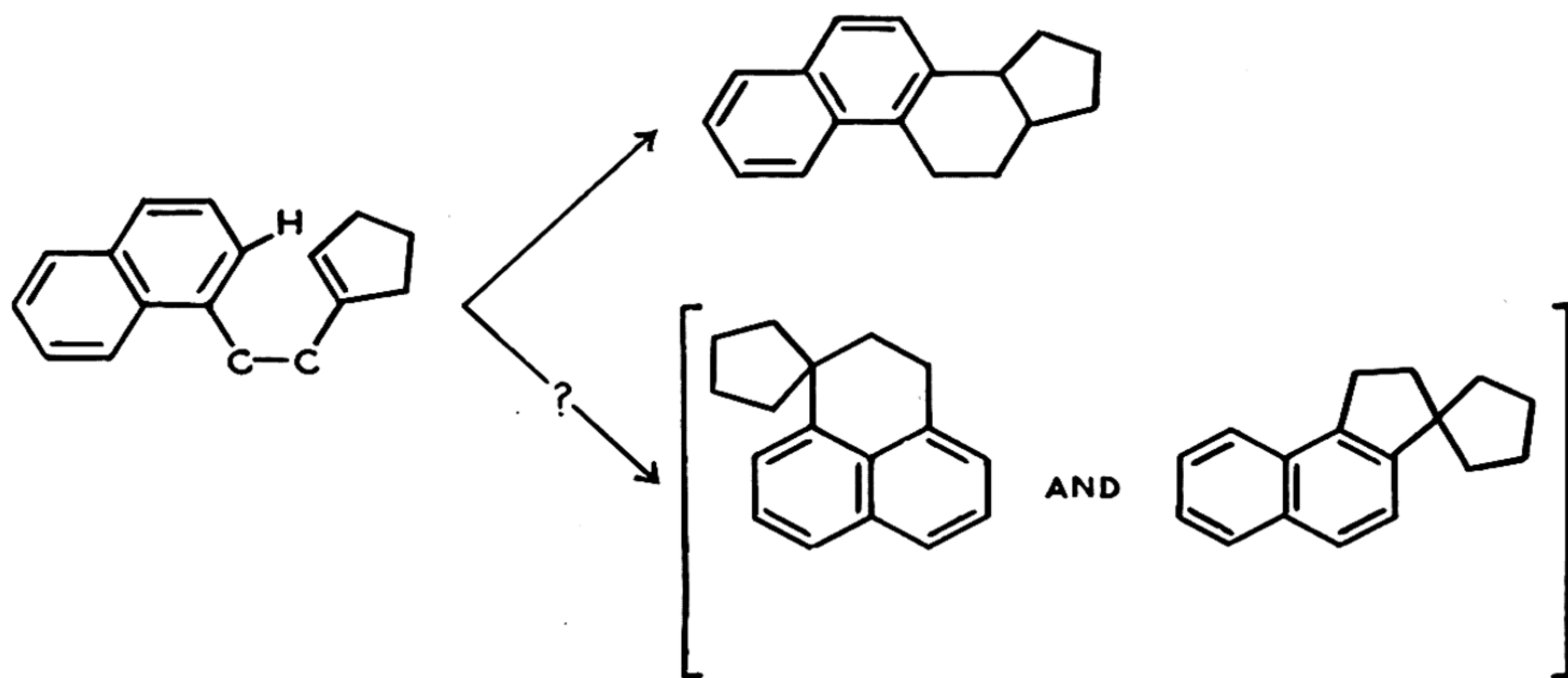
This example apparently involves an internal dehydrogenation-hydrogenation, which is a reaction effected characteristically by cold sulfuric acid.

The cyclization of 1-(*o*-biphenylyl)cyclopentene-1 (in carbon disulfide) with aluminum chloride for 5 hours at 0° resulted in the formation of 9-fluorylspirocyclopentane:²⁶

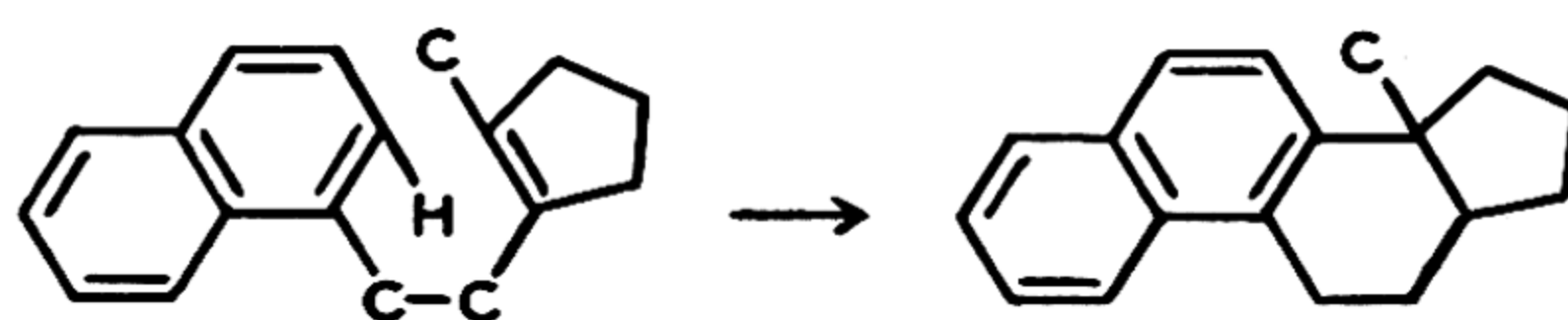


Treatment of 1-(β -1'-naphthylethyl)cyclopentene-1 (in carbon disulfide) for 24 hours at 0° with aluminum chloride gave presumably 83 per cent of *cis*- and *trans*-2,3,3a,10,11,11a-hexahydro-1-cyclopenta[*a*]phenanthrene (*i.e.*, 1,2-cyclopentano-1,2,3,4-tetrahydrophenanthrene).¹¹⁶ Subsequent investigation¹¹⁷ has indicated that the product may contain also

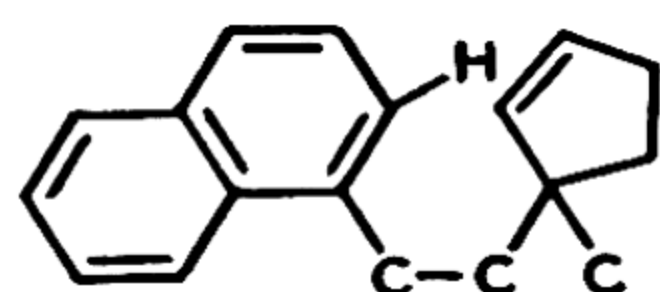
the two spiranes: 2,3-dihydro-spiro[benzonaphthene-1,1'-cyclopentane], *i.e.*, 7,8-dihydrophenalyl-7-spirocyclopentane, and 1,2-dihydro-spiro[3-benz[e]indene-3,1'-cyclopentane]:



A carbon disulfide solution of 1-methyl-2-(β -1' naphthylethyl)cyclopentene-1 was treated overnight with aluminum chloride at 0°, giving 50 per cent of 3a-methyl-2,3,3a,10,11,11a-hexahydro-1-cyclopenta[a]-phenanthrene, *i.e.*, 1-methyl-1,2-cyclopentano-1,2,3,4-tetrahydrophenanthrene:³²¹

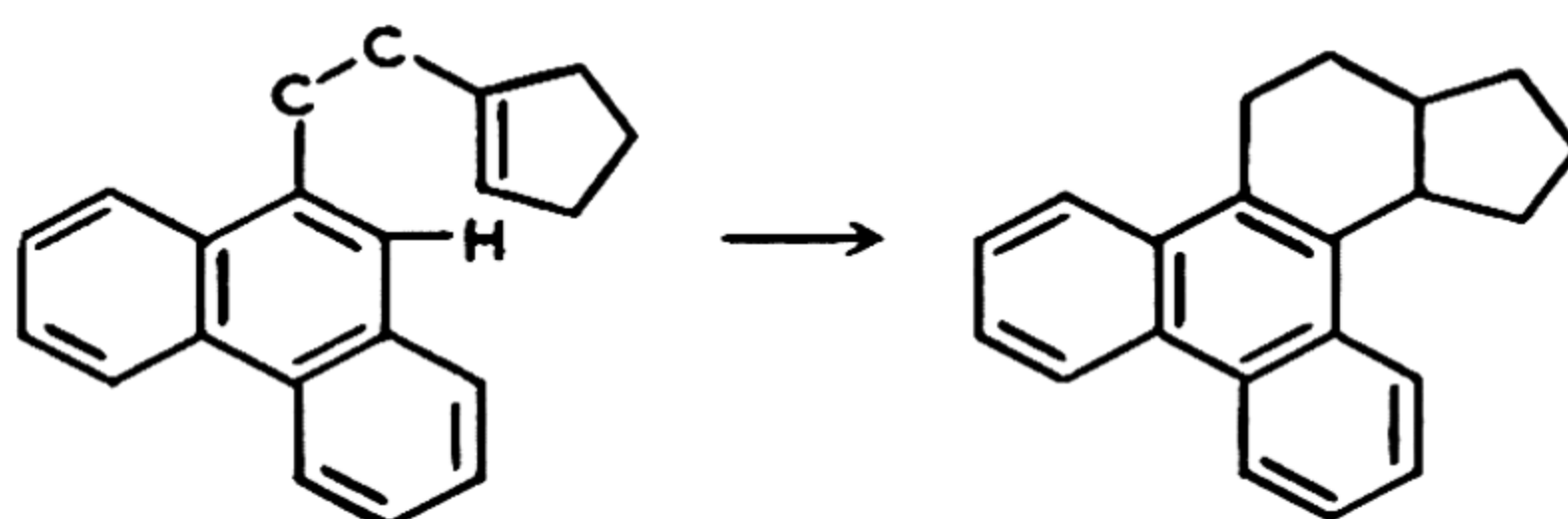


The related 1-methyl-1-(β -1'-naphthylethyl)cyclopentene-2, however, could not be cyclized by any of the reagents tried, including aluminum chloride.³²¹

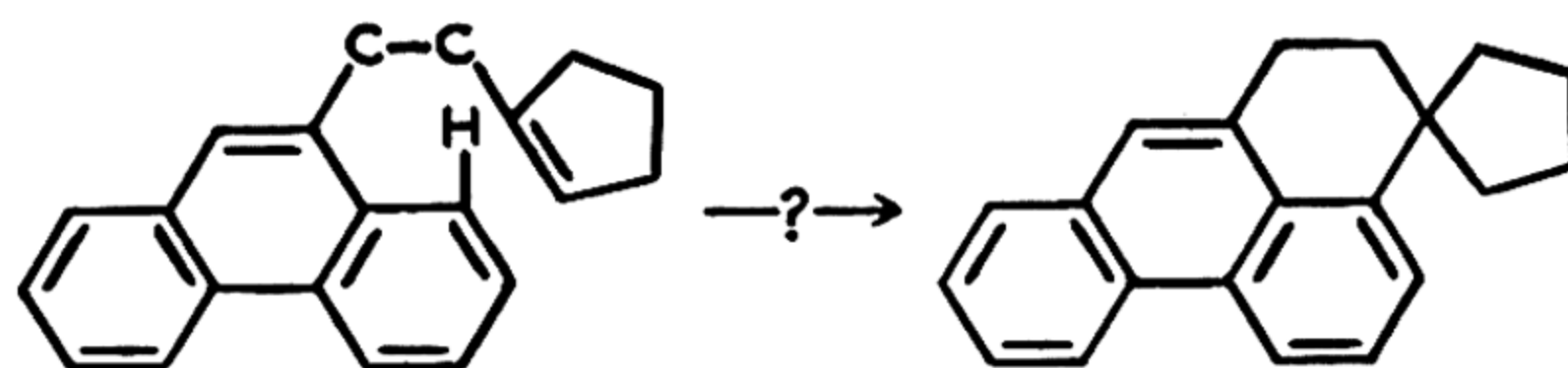


[Unisomerized to date]

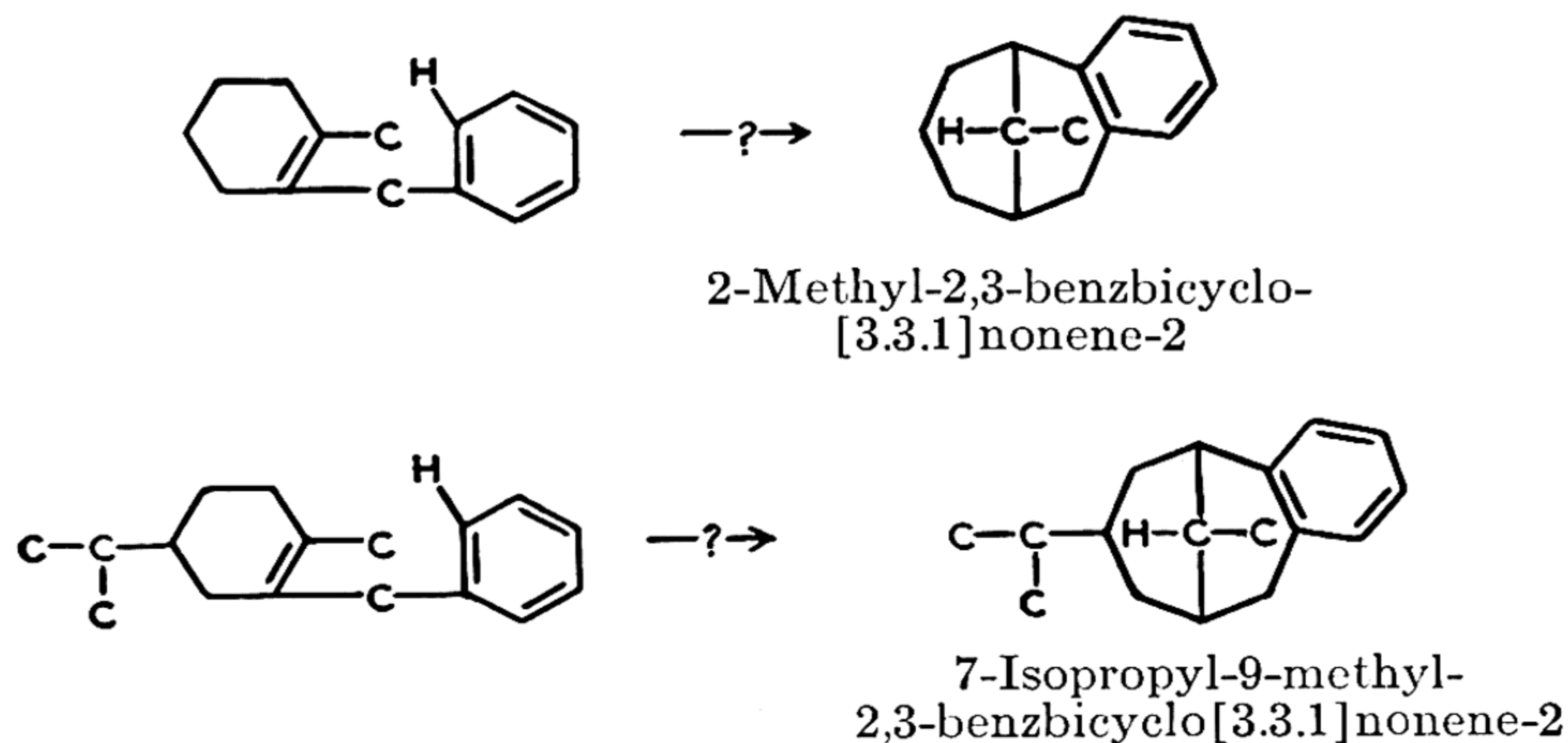
1-(β -9'-Phenanthrylethyl)cyclopentene-1, treated in carbon disulfide solution at room temperature for 12 hours with aluminum chloride, gave 49 per cent of tetrahydrocyclopentenotriphenylene:⁴⁹



Since subsequent dehydrogenation is alleged to produce a methyl-3,4-benzpyrene, the reaction has been interpreted as giving instead the dihydro-6-meso-benzanthrenespirocyclopentane.²⁵⁰ Another investigation⁴⁸ makes the structure of the isomer product even more uncertain.

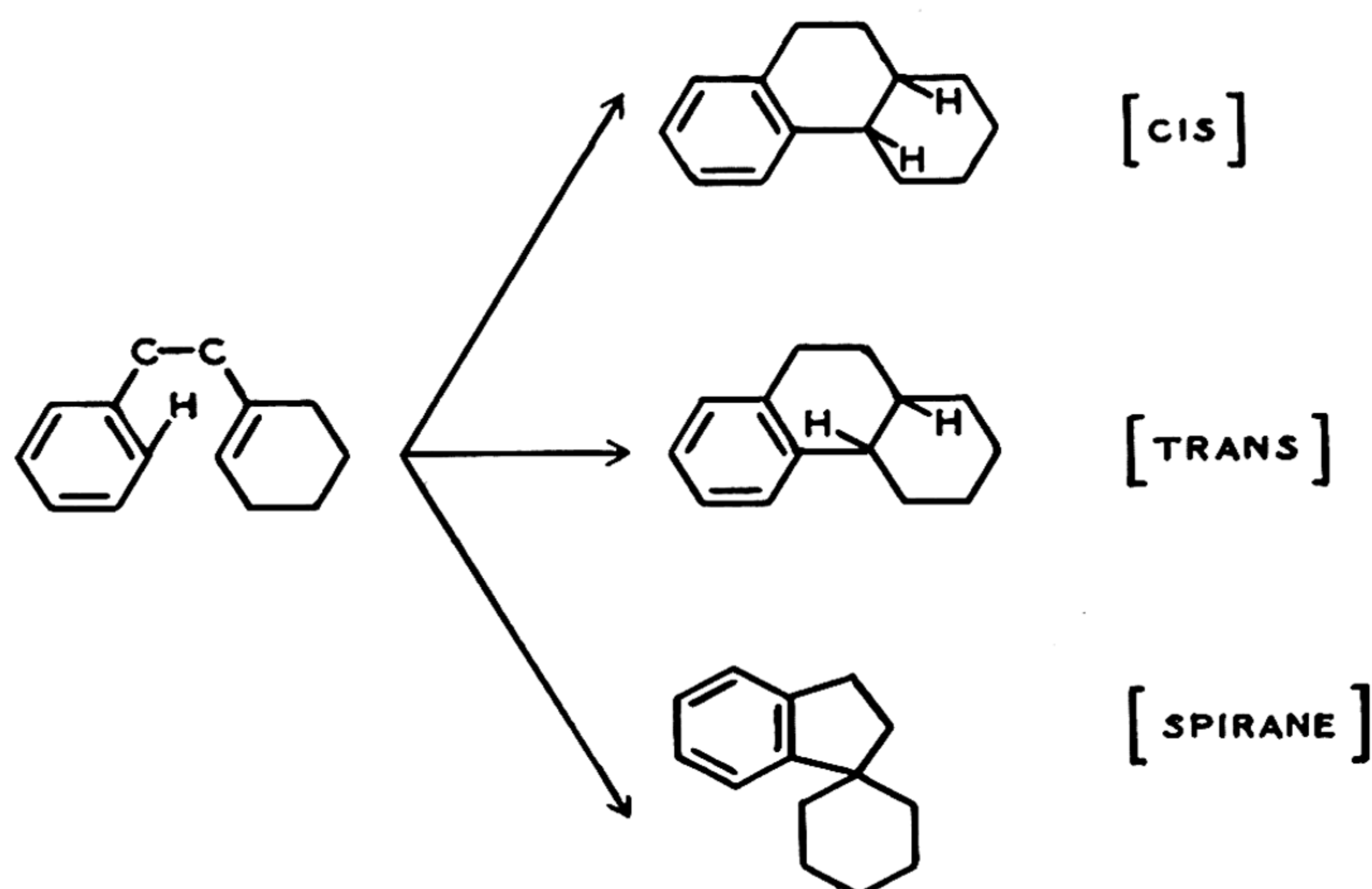


The cyclizations of 1-methyl-2-benzylcyclohexene-1 for 3 hours, and of 1-methyl-2-benzyl-4-isopropylcyclohexene-1 for 5 hours, both with aluminum chloride at 0°, gave isomers without an active double bond.¹¹⁸ It was shown that the cyclization products (70 and 75 per cent, respectively) cannot be hexahydrofluorenes, although it was not proved that there is a formation of the alternative benzbicyclononenes. Assuming the formation of the last hydrocarbons, the reactions can be given as follows:

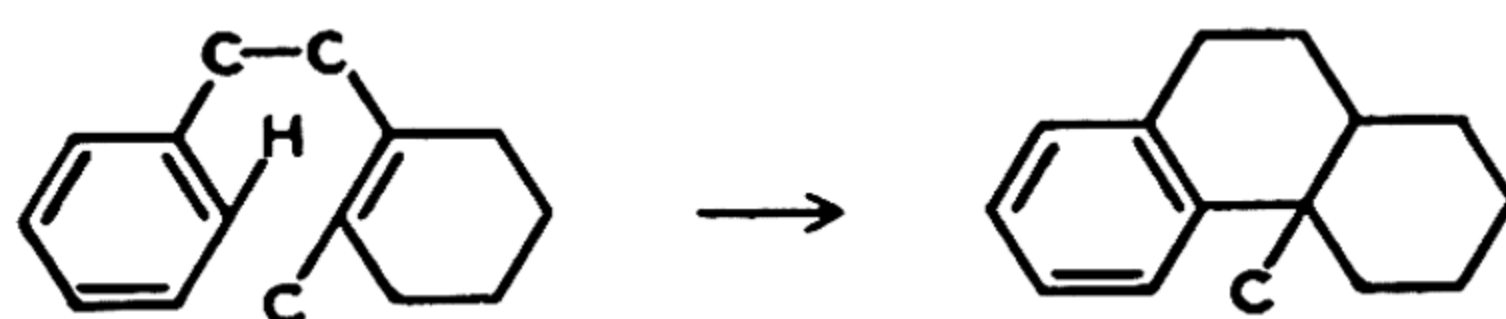


Apparently, the strainless bicyclononene system is formed in preference to the hexahydrofluorenes, but even this requires an initial isomerization into cyclohexene-5 (or -6) hydrocarbons.

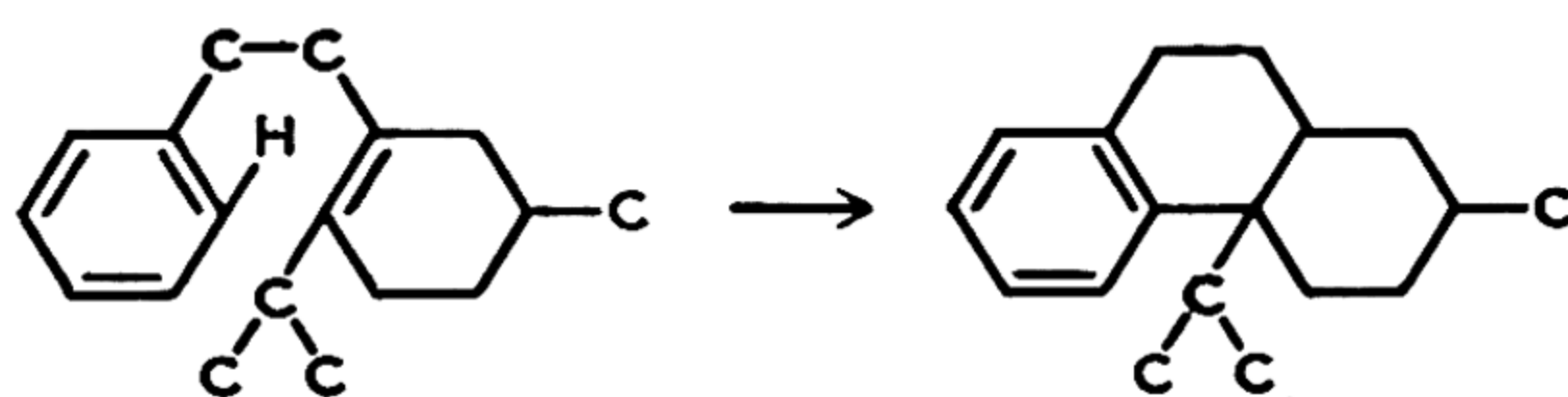
Isomerization of 1-(β -phenethyl)cyclohexene-1, in carbon disulfide solution with aluminum chloride for 6 hours,¹¹⁴ or for 24 hours,¹¹⁶ gave 1,2,3,4,4a,9,10,10a-octahydrophenanthrene. The yield in the 24-hour treatment was 49 per cent. Later work on the cyclization with aluminum chloride indicated that, depending on reaction conditions (undisclosed), the product consists of much *cis*-1,2,3,4,4a,9,10,10a-octahydrophenanthrene, less of the *trans* form, and a still smaller amount of hydrindene-spirocyclohexane.¹²⁰ 1-(β -Phenethyl)cyclohexene-1 gave 1,2,3,4,4a,9,10,10a-octahydrophenanthrene when treated with concentrated sulfuric acid⁴³⁴ or with acetic acid plus sulfuric acid:¹¹⁶



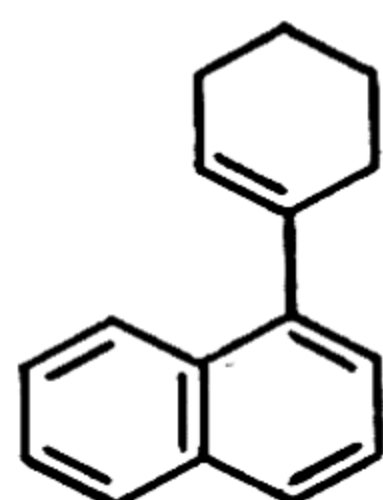
The isomerization of 1-methyl-2-(β-phenethyl)cyclohexene-1 with aluminum chloride plus carbon disulfide at 0° gave 70 per cent of 4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (*i.e.*, 12-methyl-1,2,3,4,9,10,11,12-octahydrophenanthrene):³²¹



The cyclization of 1-isopropyl-2-(β-phenethyl)-4-methylcyclohexene-1 into 2-methyl-4a-isopropyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (*i.e.*, 2-methyl-12-isopropyl-1,2,3,4,9,10,11,12-octahydrophenanthrene) occurred almost quantitatively in the presence of concentrated sulfuric acid, but not at all with 90-per cent sulfuric acid in the cold:⁴²⁷

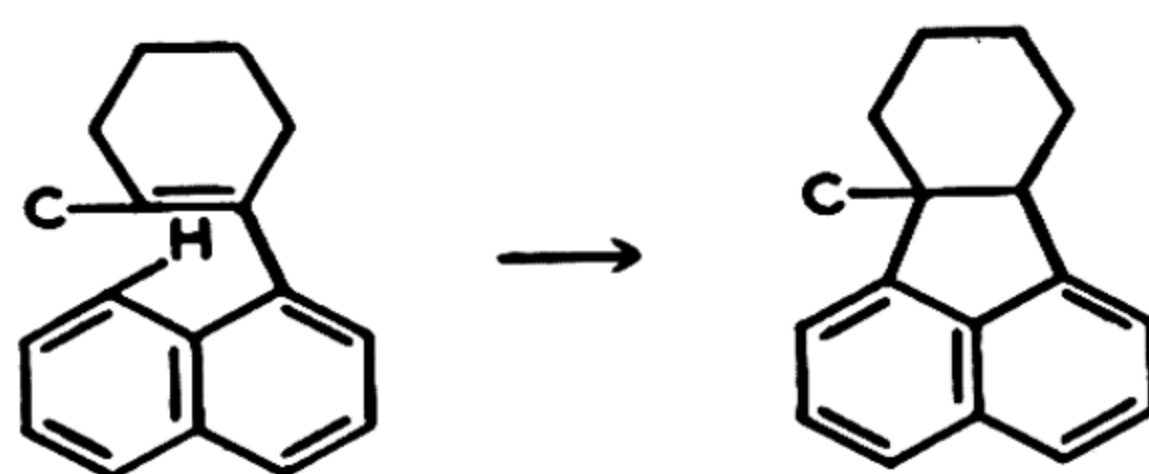


An attempt at the cyclization of 1-(1'-naphthyl)cyclohexene-1 was unsuccessful.¹²¹

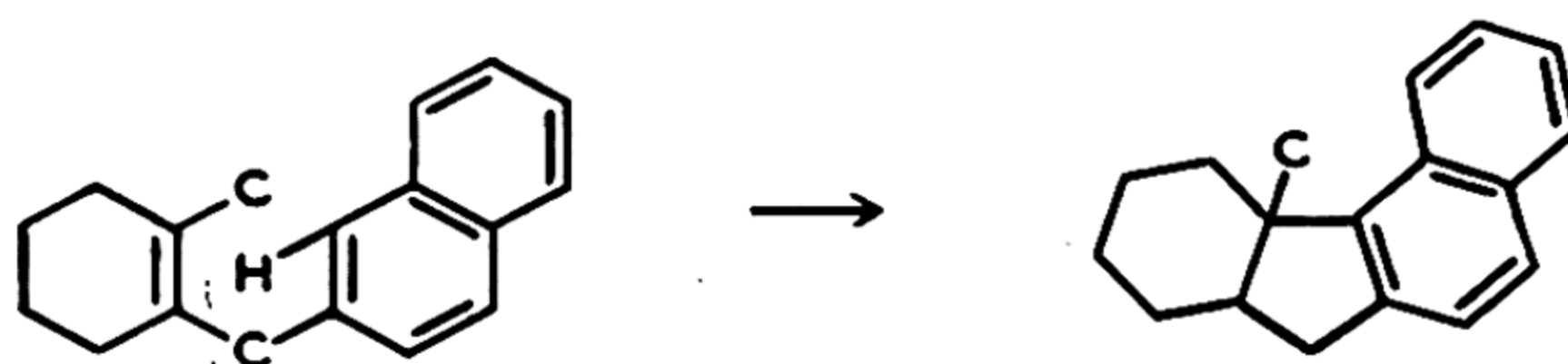


[Unisomerized to date]

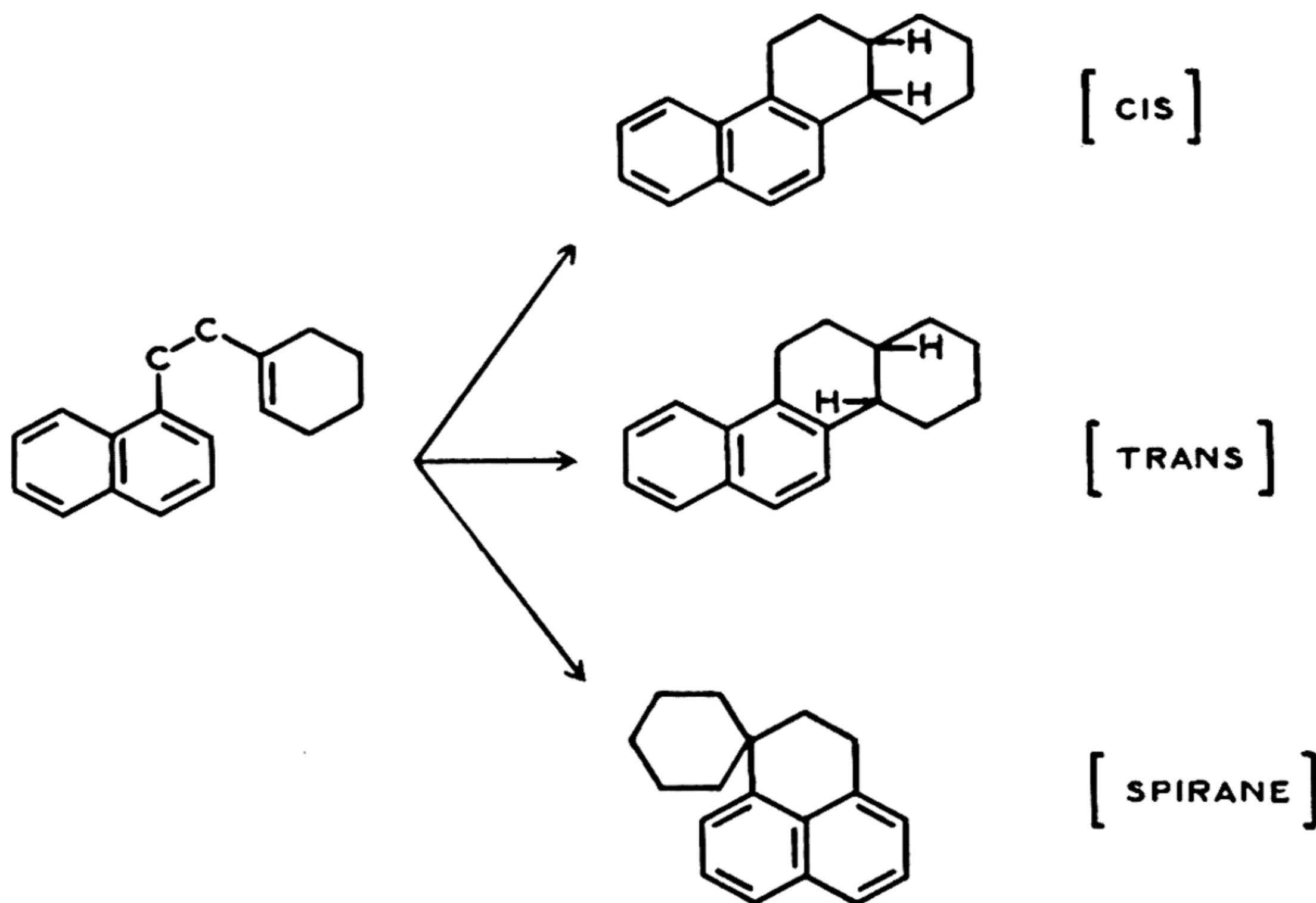
1-Methyl-2-(1'-naphthyl)cyclohexene-1 when treated with aluminum chloride plus carbon disulfide at 0° was cyclized to 6b-methyl-6b,7,8,9,-10,10a-hexahydrofluoranthene: ¹²¹



Treatment of 1-methyl-2-(2'-naphthylmethyl)cyclohexene-1, in carbon disulfide solution for 6 hours at 0° with aluminum chloride, gave 47 per cent of 11a-methyl-7a,8,9,10,11,11a-hexahydro-7-benzo[c]fluorene, *i.e.*, 7a,8,9,10,11,11a-hexahydro-11a-methyl-3,4-benzofluorene: ¹¹³



The action of aluminum chloride upon 1-(β-1'-naphthylethyl)-cyclohexene-1 in carbon disulfide at 0° led to a mixture of *cis*- and *trans*-1,2,3,4,4a,11,12,12a-octahydrochrysenes and 2,3-dihydro-spiro[benzonaphthene-1,1'-cyclohexane], *i.e.*, 7,8-dihydrophenalyl-7-spirocyclohexane: ¹¹⁷

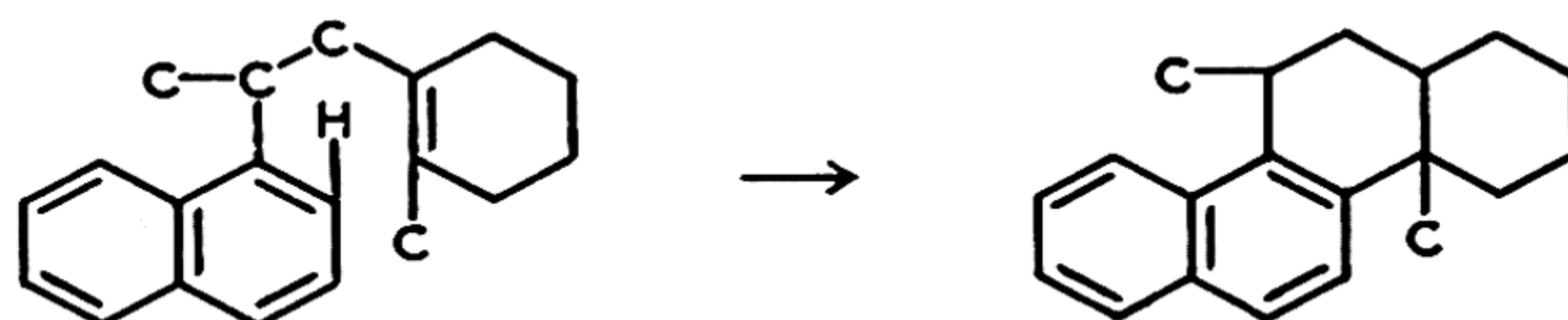


The cyclization of 1-methyl-2-(β-1'-naphthylethyl)cyclohexene-1, *i.e.*, 1-(β-[2-methylcyclohex-1-en-1-yl]ethyl)naphthalene, in carbon disulfide solution for 7 hours at 0° with aluminum chloride, gave 60 per

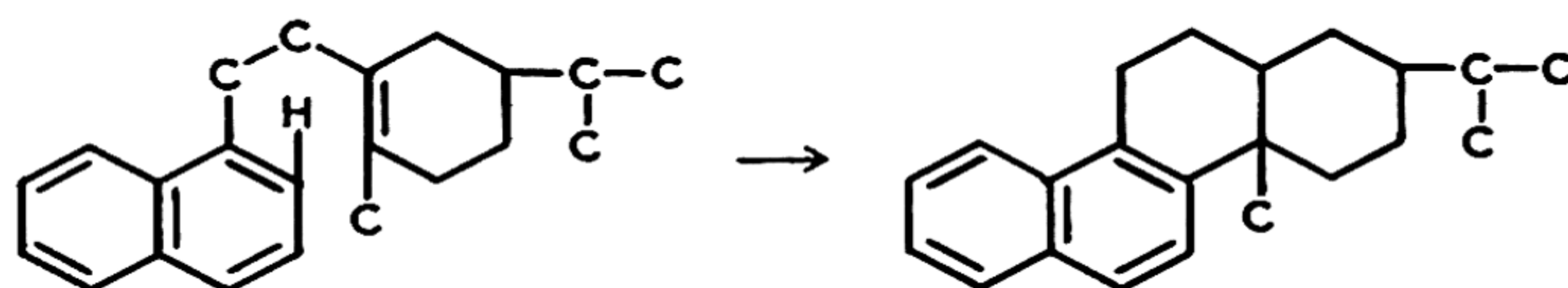
cent of 4a-methyl-1,2,3,4,4a,11,12,12a-octahydrochrysene, formerly named 1,2,2a,3,4,5,6,6a-octahydro-6a-methylchrysene:¹¹⁵



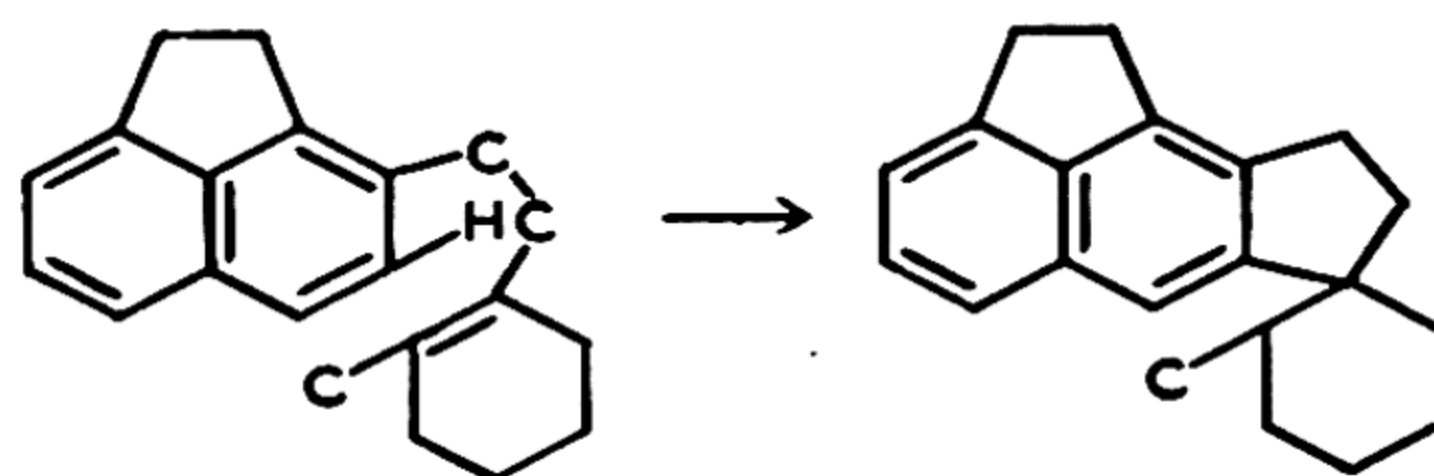
The reaction of 1-methyl-2-(β -1'-naphthyl-*n*-propyl)cyclohexene-1, *i.e.*, 1-(2-methylcyclohex-1-en-1-yl)-2-(α -naphthyl)propane or 1-(β -[2-methylcyclohex-1-en-1-yl]isopropyl)naphthalene, with aluminum chloride plus carbon disulfide for 21 hours at 0°, yielded 72 per cent of 4a,11-dimethyl-1,2,3,4,4a,11,12,12a-octahydrochrysene ("5,10a-dimethyl - as-octahydrochrysene"): ¹⁸⁶



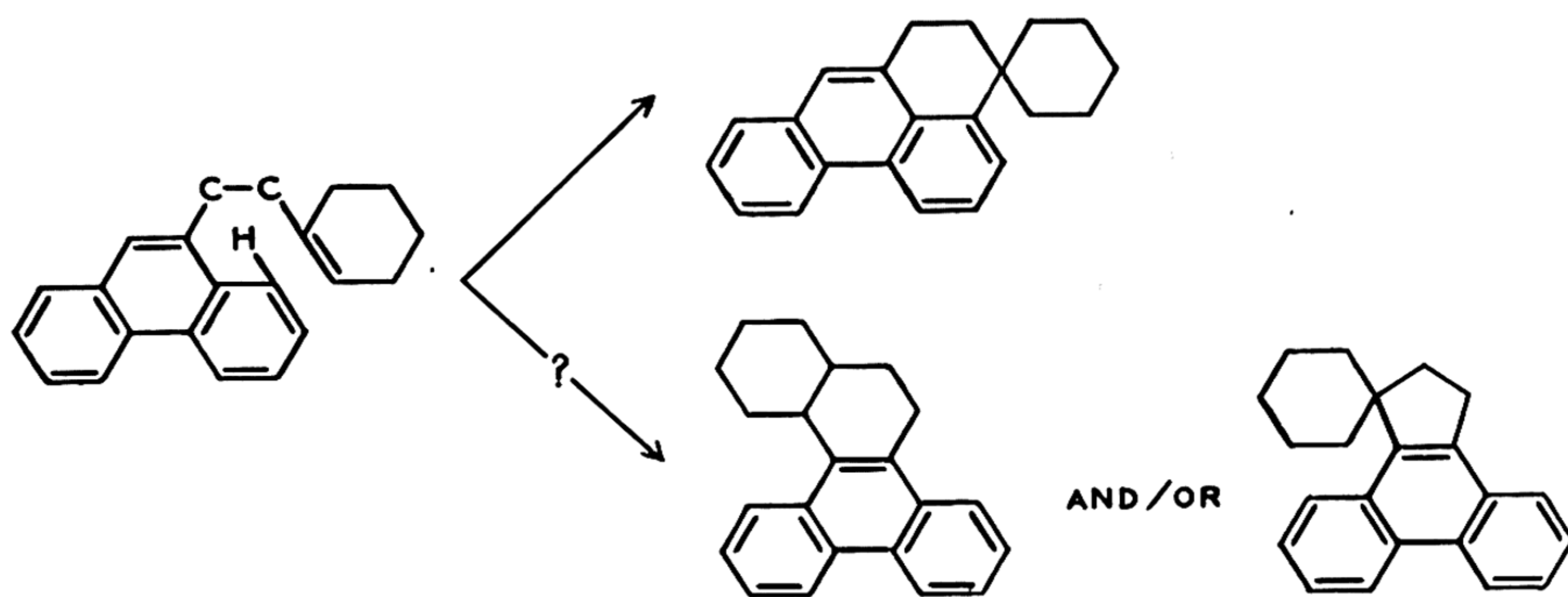
Cyclization of 1-methyl-2-(β -1'-naphthylethyl)-4-isopropylcyclohexene-1, *i.e.*, 1-(β -[1-methyl-4-isopropylcyclohex-1-en-2-yl]ethyl)-naphthalene, with aluminum chloride plus carbon disulfide for 24 hours at 0°, gave 2-isopropyl-4a-methyl-1,2,3,4,4a,11,12,12a-octahydrochrysene:¹²³



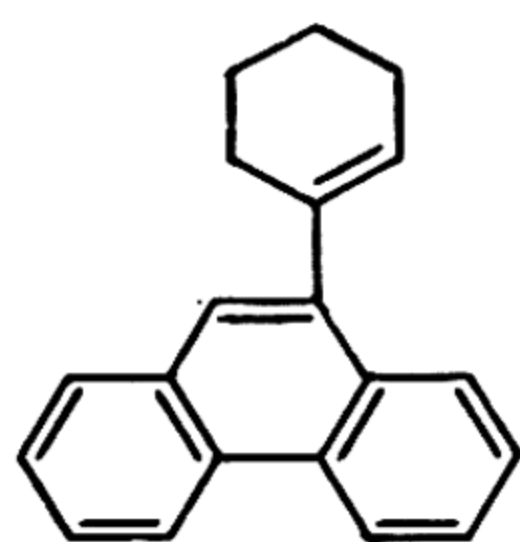
Treatment of 1-methyl-2-(β -3'-acenaphthylethyl)cyclohexene-1, *i.e.*, 3-(β -[2-methylcyclohex-1-en-1-yl]ethyl)acenaphthene, with aluminum chloride plus carbon disulfide (for 21 hours at 0°) gave 8,9-dihydro-2'-methyl-spiro[β -acenaphthindan-3,1'-cyclohexane]: ¹¹⁵



An attempted cyclization of 1-(β -9'-phenanthrylethyl)cyclohexene-1 into octahydro-1,2,3,4-dibenzphenanthrene, by aluminum chloride plus carbon disulfide at 0°, gave a spirane, probably a dihydrobenzanthrene-spirocyclohexane.²⁵⁰ The formation of dihydrocyclopenta[*l*]phenanthrenespirocyclohexane, however, was not excluded:

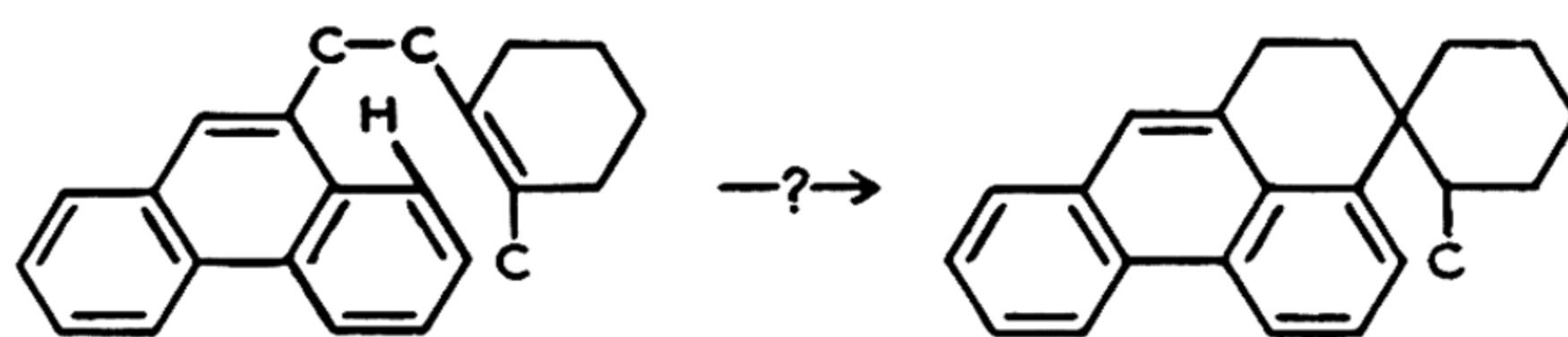


Cyclization of 9-cyclohexenylphenanthrene into 5,6-benzofluoranthene by treatment with carbon disulfide and aluminum chloride for 24 hours at 0° was a failure.⁴⁷

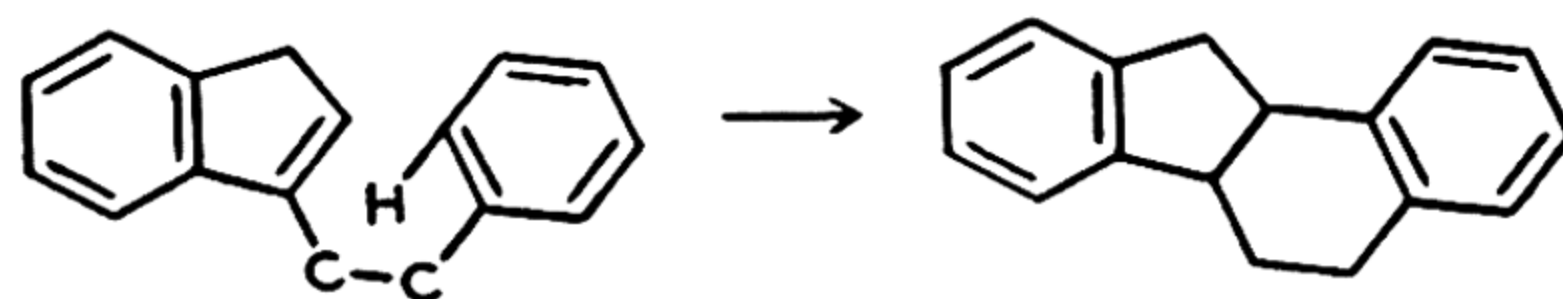


[Unisomerized to date]

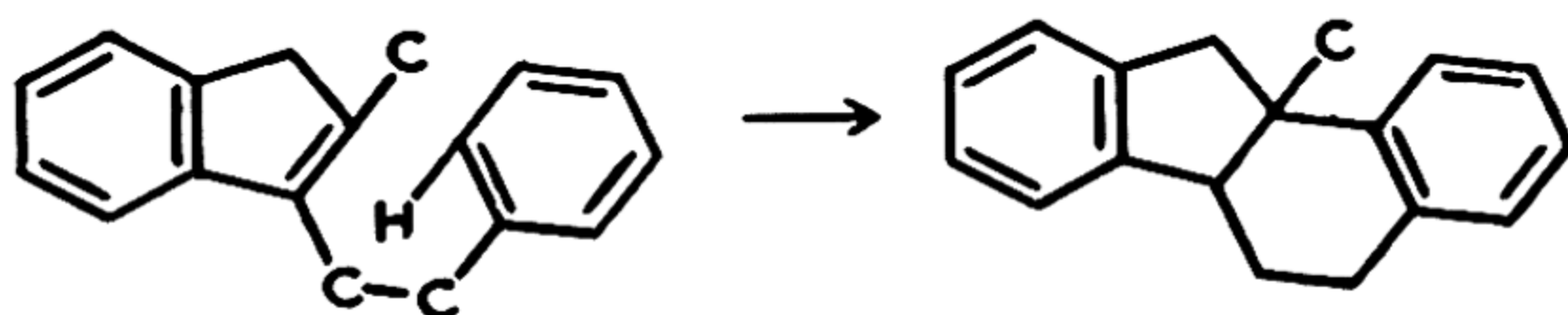
Isomerization of 1-methyl-2-(β-9'-phenanthrylethyl)cyclohexene-1 with aluminum chloride did not always give satisfactory results, but treatment with hydrogen chloride plus stannic chloride gave 80 per cent of a presumable spirane.⁴⁵ The structure of the last product may be that of a dihydrobenzanthrenespiromethylcyclohexane.



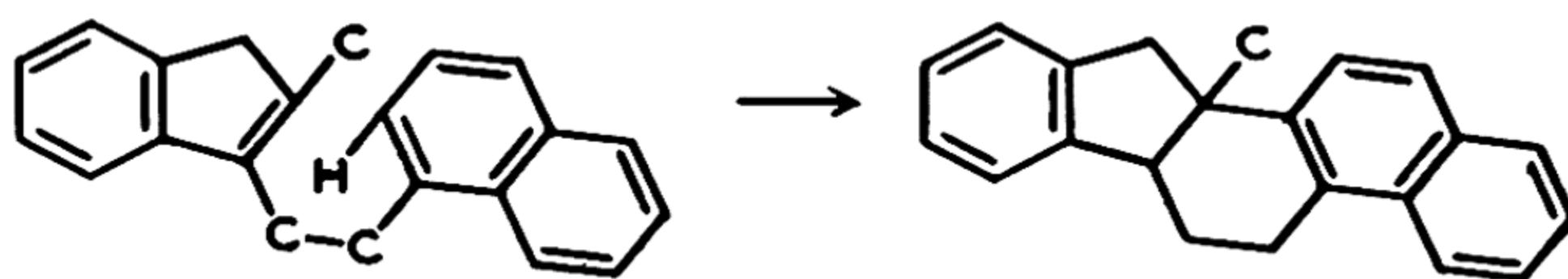
The reaction of 3-(β-phenethyl)indene with aluminum chloride and carbon disulfide at 0°, or with acetic acid containing sulfuric acid at 100°, resulted respectively in 18 and 16 per cent of 5,6,6a,11a-tetrahydrochrysofluorene:¹¹⁷



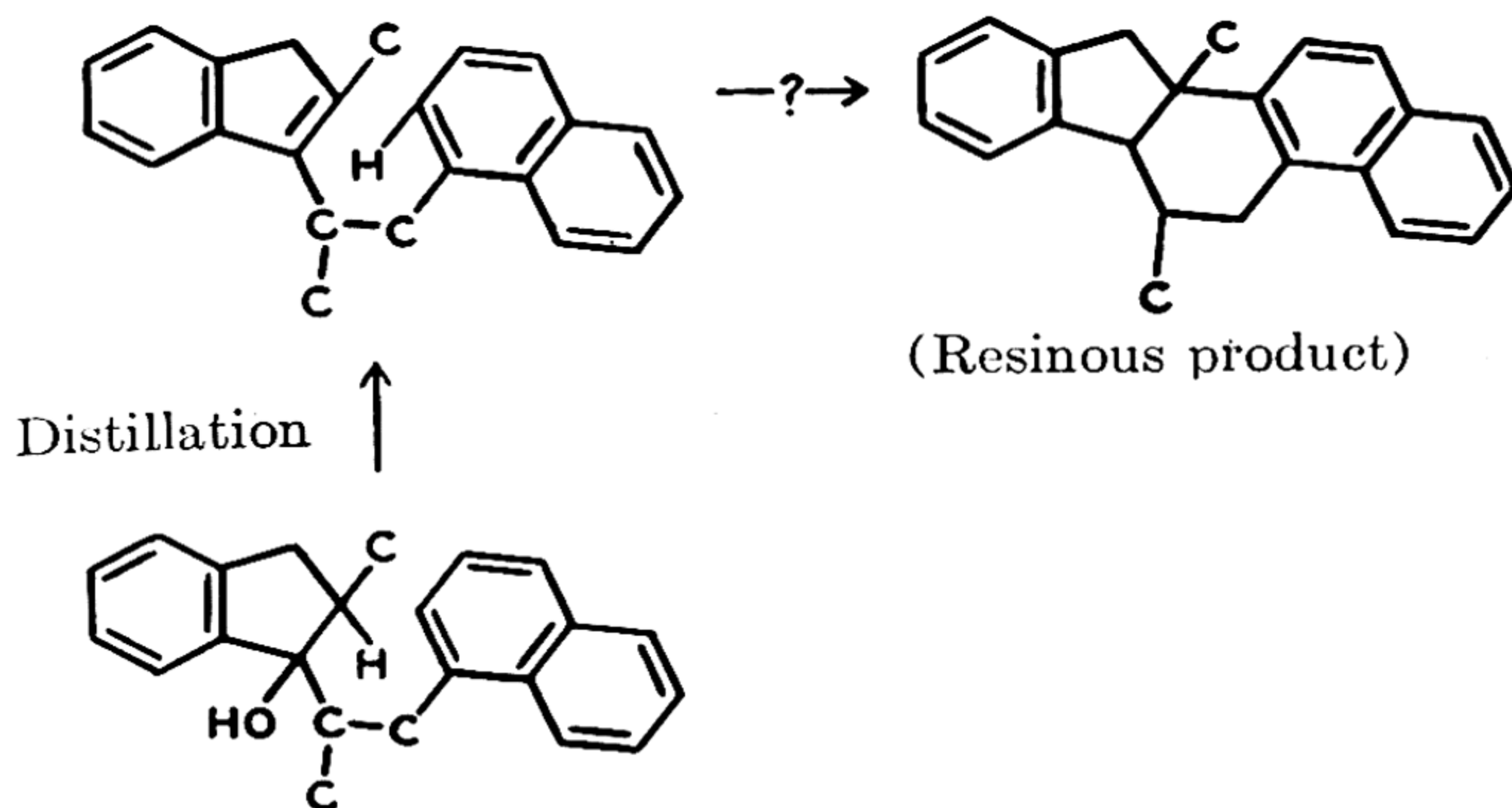
Treatment of 2-methyl-3-(β-phenethyl)indene (in carbon disulfide solution with aluminum chloride for 3 hours at 0°) yielded 82 per cent of 5,6,6a,11a-tetrahydro-11a-methylchrysofluorene:¹¹⁹



The cyclization of 2-methyl-3-(β -1'-naphthylethyl)indene with aluminum chloride and carbon disulfide (for 3 hours at 0°) resulted in 77.1 per cent of crude and 27.2 per cent of pure 11a-methyl-5,6,6a,11a-tetrahydro-11-naphtho[2,1-a]fluorene, *i.e.*, 10-methyl-3,4,10,11-tetrahydro-2',1'-naphtha-1,2-fluorene:²⁵

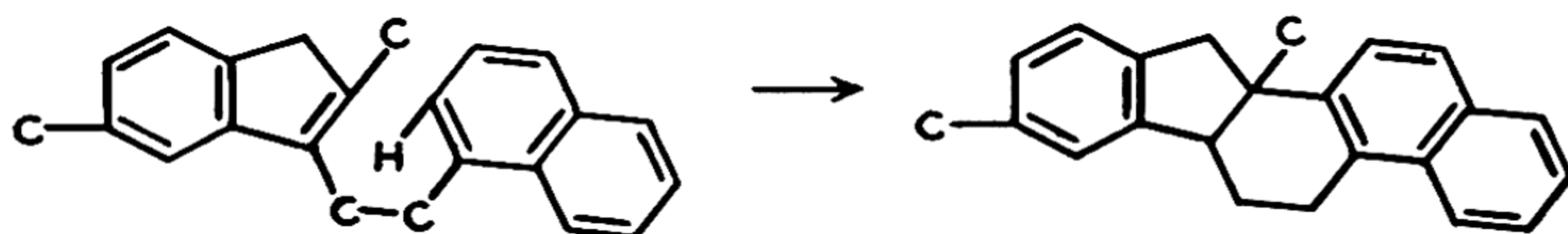


The formation of a resinous liquor by the treatment of a distillation product from 1-(β -1'-naphthylisopropyl)-2-methyl-indanol-1, with aluminum chloride plus carbon disulfide at 2-3° C., can be taken as the formation of 6,11a-dimethyl-5,6,6a,11a-tetrahydro-11-naphtho[2,1-a]fluorene (*i.e.*, 4,10-dimethyl-3,4,10,11-tetrahydro-2',1'-naphtha-1,2-fluorene) from 2-methyl-3-(β -1'-naphthylisopropyl)indene [*i.e.*, 1-(α -naphthyl)-2-(2-methylindenyl-3)-propane or 1-(β -[2-methylindenyl-3]propyl)-naphthalene]:²⁵

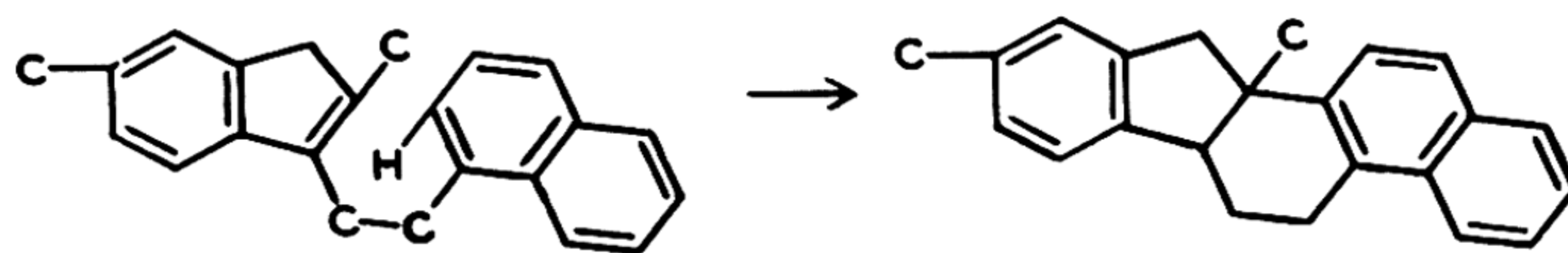


A selenium dehydrogenation was conducted upon the resinous product; its results confirm the foregoing interpretation of the cyclization.

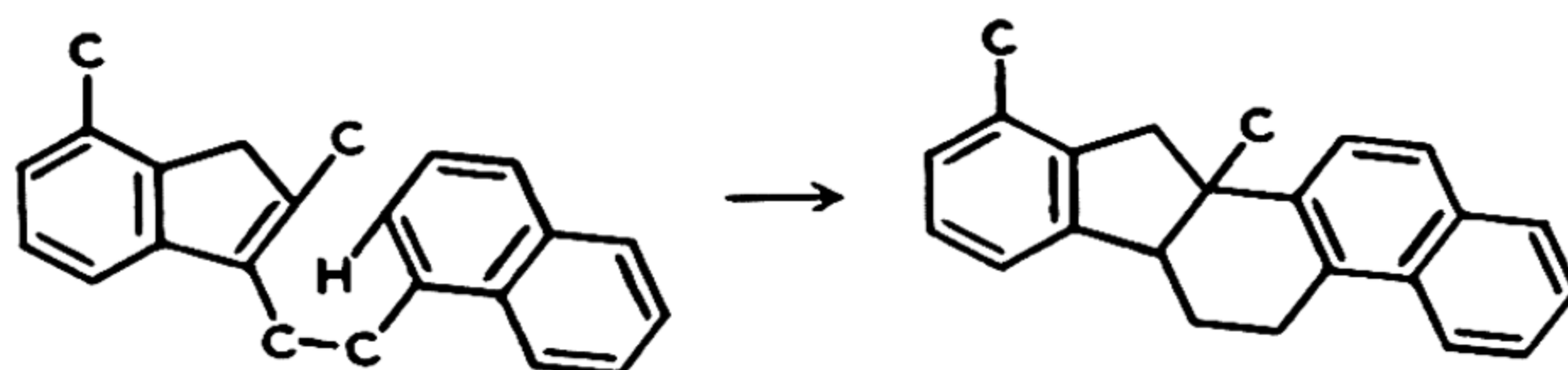
The treatment of 2,5-dimethyl-3-(β -1'-naphthylethyl)indene with aluminum chloride plus carbon disulfide for 3 hours at 0° gave 75.5 per cent of crude and 18.9 per cent of pure 8,11a-dimethyl-5,6,6a,11a-tetrahydro-11-naphtho[2,1-a]fluorene (*i.e.*, 6,10-dimethyl-3,4,10,11-tetrahydro-2',1'-naphtha-1,2-fluorene):²⁵



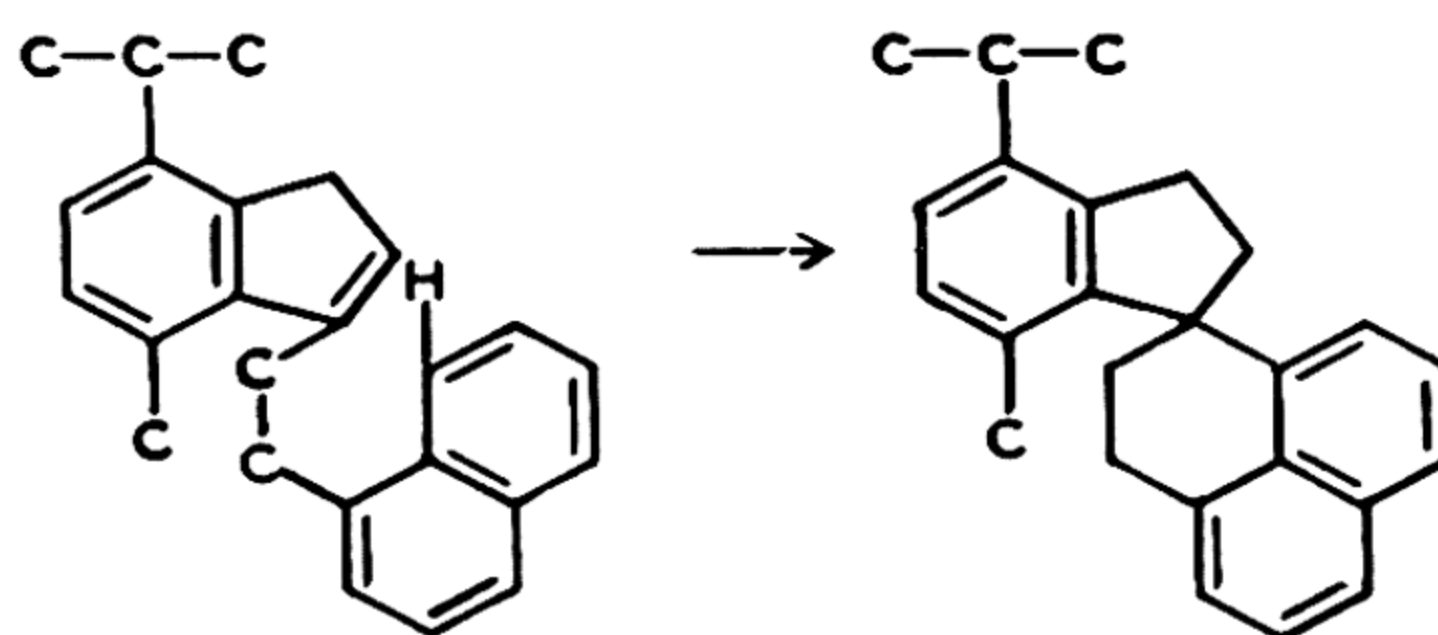
The isomerization of an impure (88.9 per cent pure ?) 2,6-dimethyl-3-(β -1'-naphthylethyl)indene with aluminum chloride plus carbon disulfide for 3 hours at 0° gave 67.5 per cent of crude (corrected for known impurity) and 5.0 per cent of pure 9,11a-dimethyl-5,6,6a,11a-tetrahydro-11-naphtho[2,1-a]fluorene (*i.e.*, 7,10-dimethyl-3,4,10,11-tetrahydro-2',1'-naphtha-1,2-fluorene):²⁵



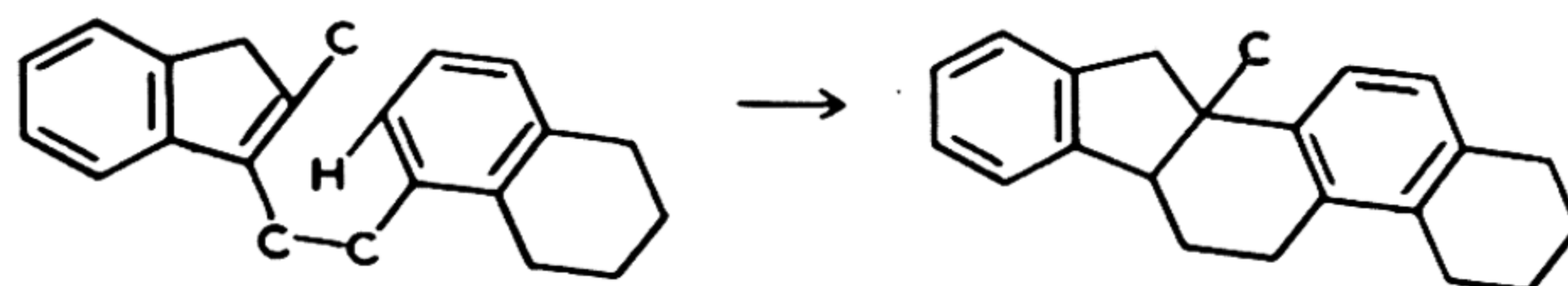
The reaction of 2,7-dimethyl-3-(β -1'-naphthylethyl)indene with aluminum chloride plus carbon disulfide, for 3 hours at 0°, resulted in the formation of 80.9 per cent of crude and 19.1 per cent of pure 10,11a-dimethyl-5,6,6a,11a-tetrahydro-11-naphtho[2,1-a]fluorene (*i.e.*, 8,10-dimethyl-3,4,10,11-tetrahydro-2',1'-naphtha-1,2-fluorene):²⁵



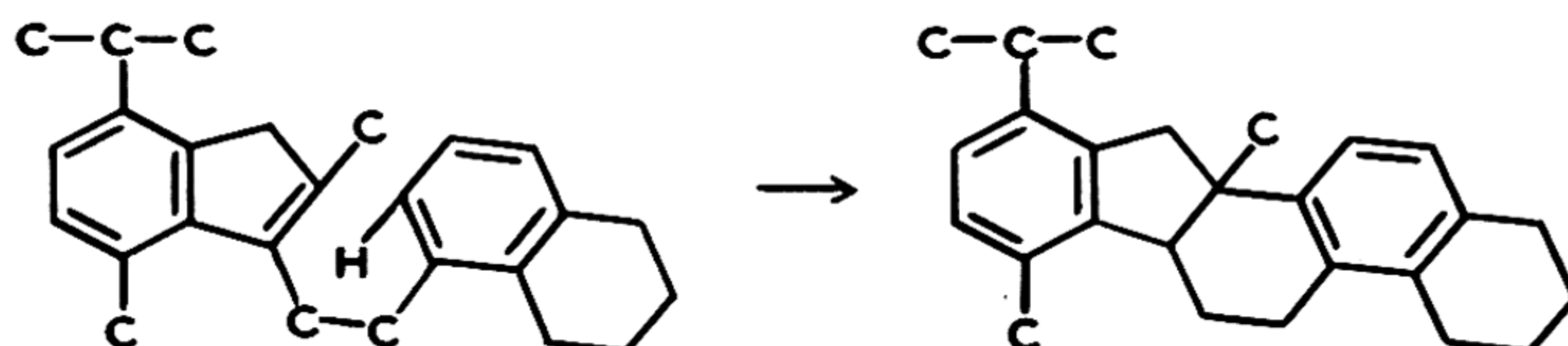
3-(β -1'-Naphthylethyl)-4-methyl-7-isopropylindene was isomerized by aluminum chloride plus carbon disulfide (within 4 hours at 0°) into 2,3-dihydro-4'-isopropyl-7'-methyl-spiro[benzonaphthene-1,1'-indan]:¹¹⁹



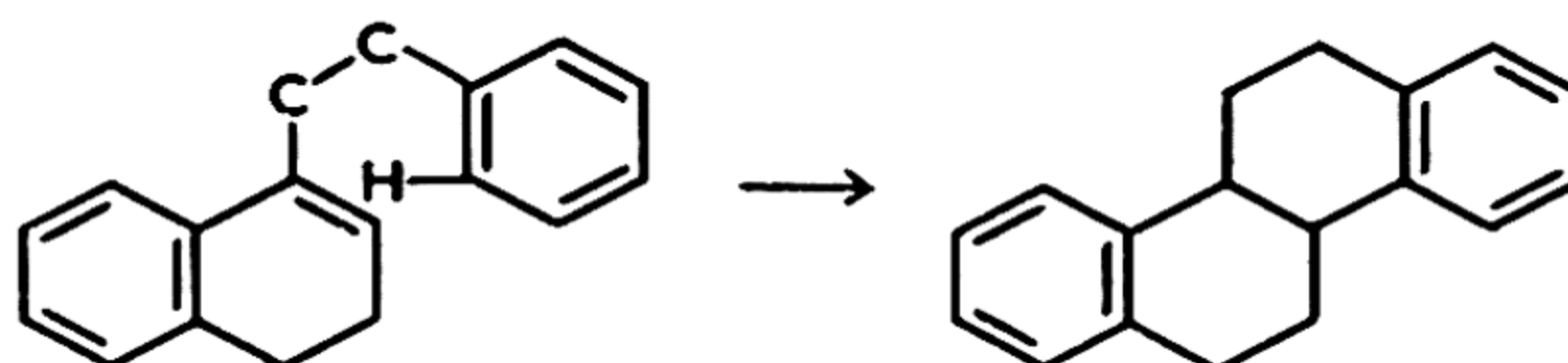
Treatment of 2-methyl-3-(β -[5,6,7,8-tetrahydro-1-naphthyl]-ethyl)-indene [*i.e.*, 1,2,3,4-tetrahydro-5-(β -[2-methyl-3-indenyl]-ethyl)naphthalene] with aluminum chloride plus carbon disulfide for 3 hours at 0°, gave 80 per cent of 1,2,3,4,5,6,6a,11a-octahydro-11a-methyl-11-naphtho[2,1-a]fluorene.¹¹⁹ The same product resulted in a cyclization at 100° with acetic acid containing sulfuric acid:¹¹⁹



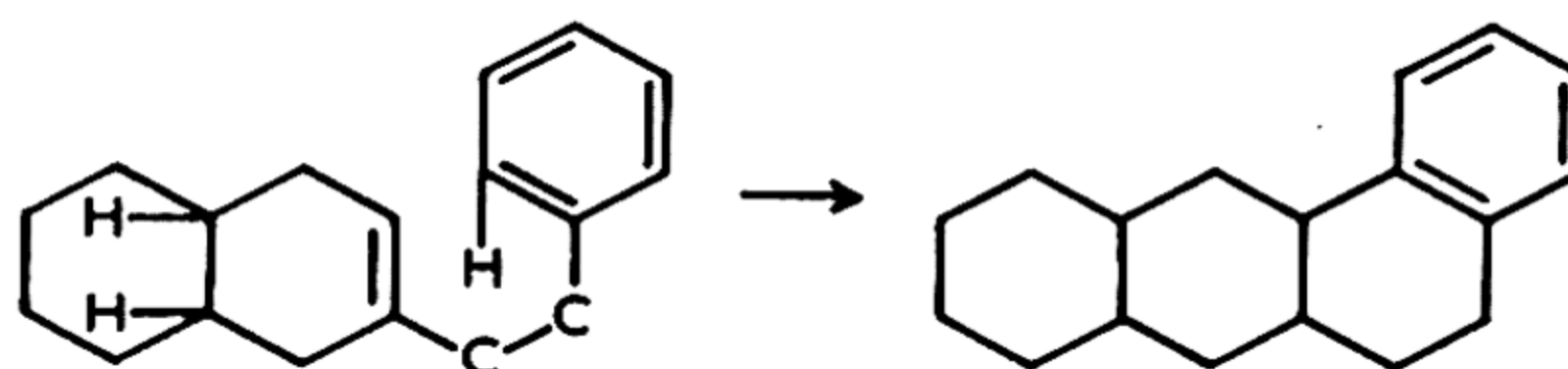
Isomerization of 2,4-dimethyl-3-(β -[5,6,7,8-tetrahydro-1-naphthyl]-ethyl)-7-isopropylindene, *i.e.*, 1,2,3,4-tetrahydro-5-(β -[2,4-dimethyl-7-isopropyl-3-indenyl]ethyl)naphthalene, with aluminum chloride plus carbon disulfide for 3 hours at 0°, gave 75 per cent of 1,2,3,4,5,6,6a,11a-octahydro-7,11a-dimethyl-10-isopropyl-11-naphtho [2,1-a] fluorene.¹¹⁹ The same product results in a cyclization at 100° with acetic acid containing sulfuric acid:¹¹⁹



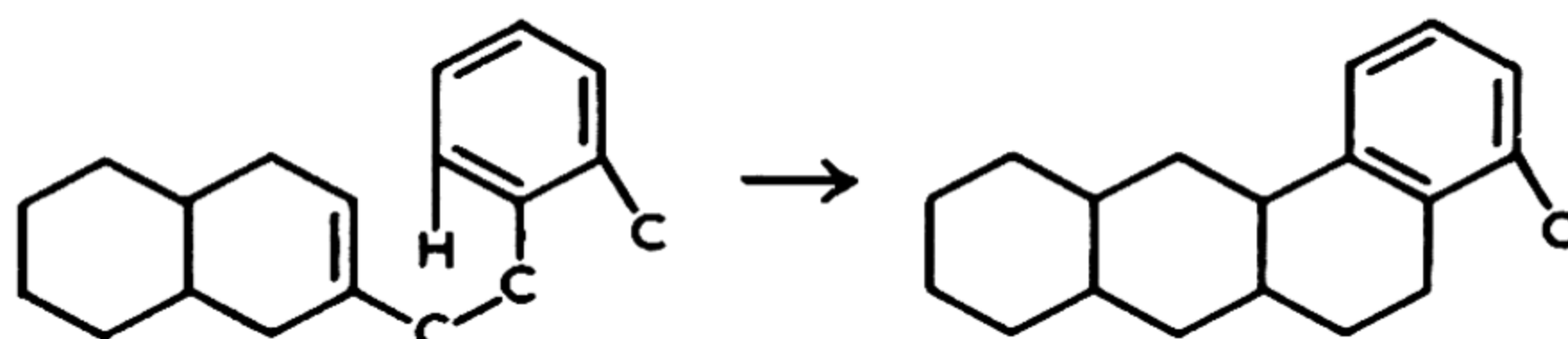
The action of aluminum chloride upon 1-(β -phenethyl)-3,4-dihydronaphthalene (in carbon disulfide at 0°) gave only 0.5 per cent of 4b,5,6,10b,11,12-hexahydrochrysene, along with 53.2 per cent of 1-(β -phenethyl)-naphthalene as a dehydrogenation by-product:¹¹⁷



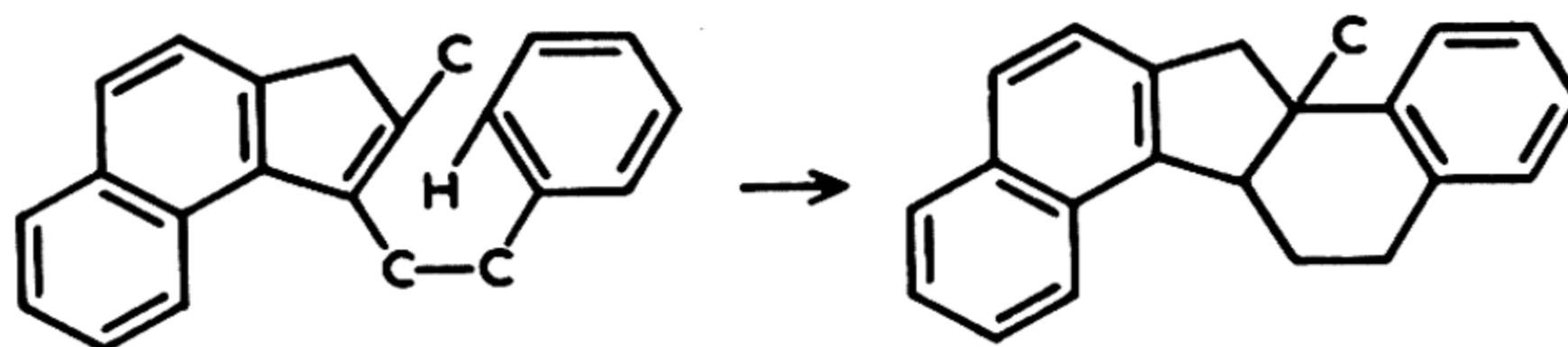
Cyclization of 2-(β -phenethyl)-*cis*- Δ^2 -octalin with aluminum chloride plus carbon disulfide for 3 hours at 0°, and then for several hours at room temperature, gave some 83 per cent of dodecahydro-1,2-benzanthracene.¹²² A previous experiment resulted in a total of 34.9 per cent of *cis* and *trans* isomerides of dodecahydro-1,2-benzanthracene:¹¹⁷



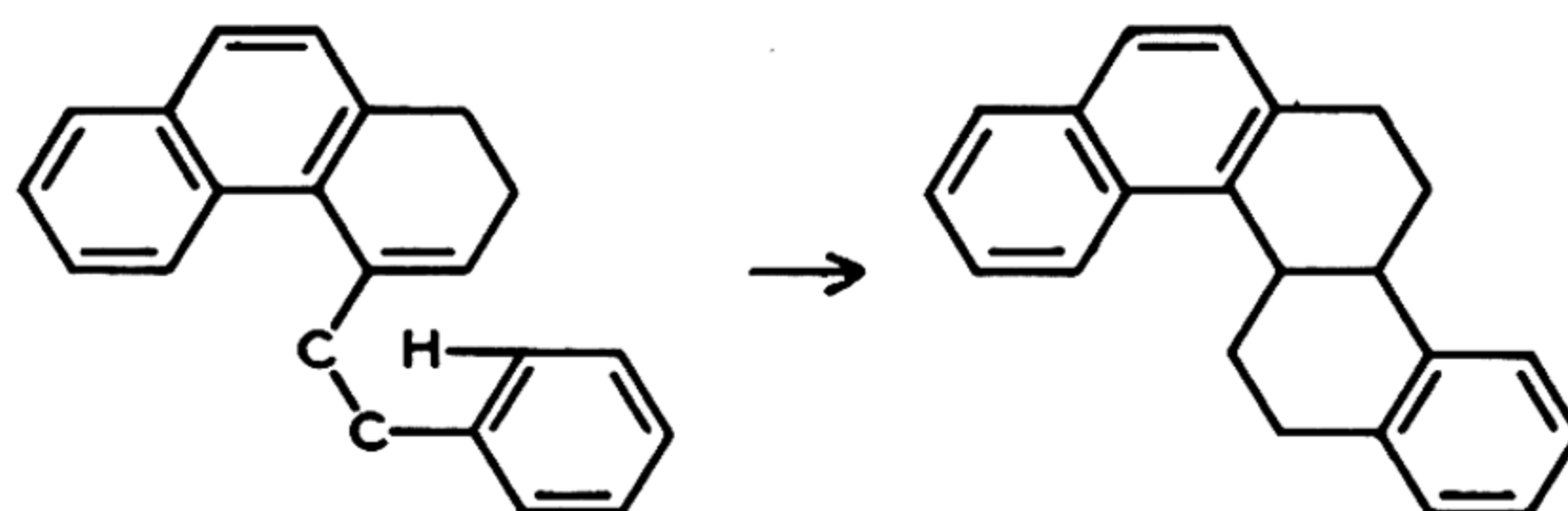
Gradual addition of aluminum chloride at 0° to a carbon disulfide solution of 2-(β -*o*-tolylethyl)- Δ^2 -octalin, *i.e.*, 1,4,4a,5,6,7,8,8a-octahydro-2-(*o*-methyl- β -phenethyl)naphthalene, resulted in a 7.1 per cent formation of 4'-methyldodecahydro-1,2-benzanthracene, *i.e.*, 4-methyl-5,6,6a,7,7a,8,9,10,11,11a,12,12a-dodecahydrobenz[a]anthrene:¹²⁴



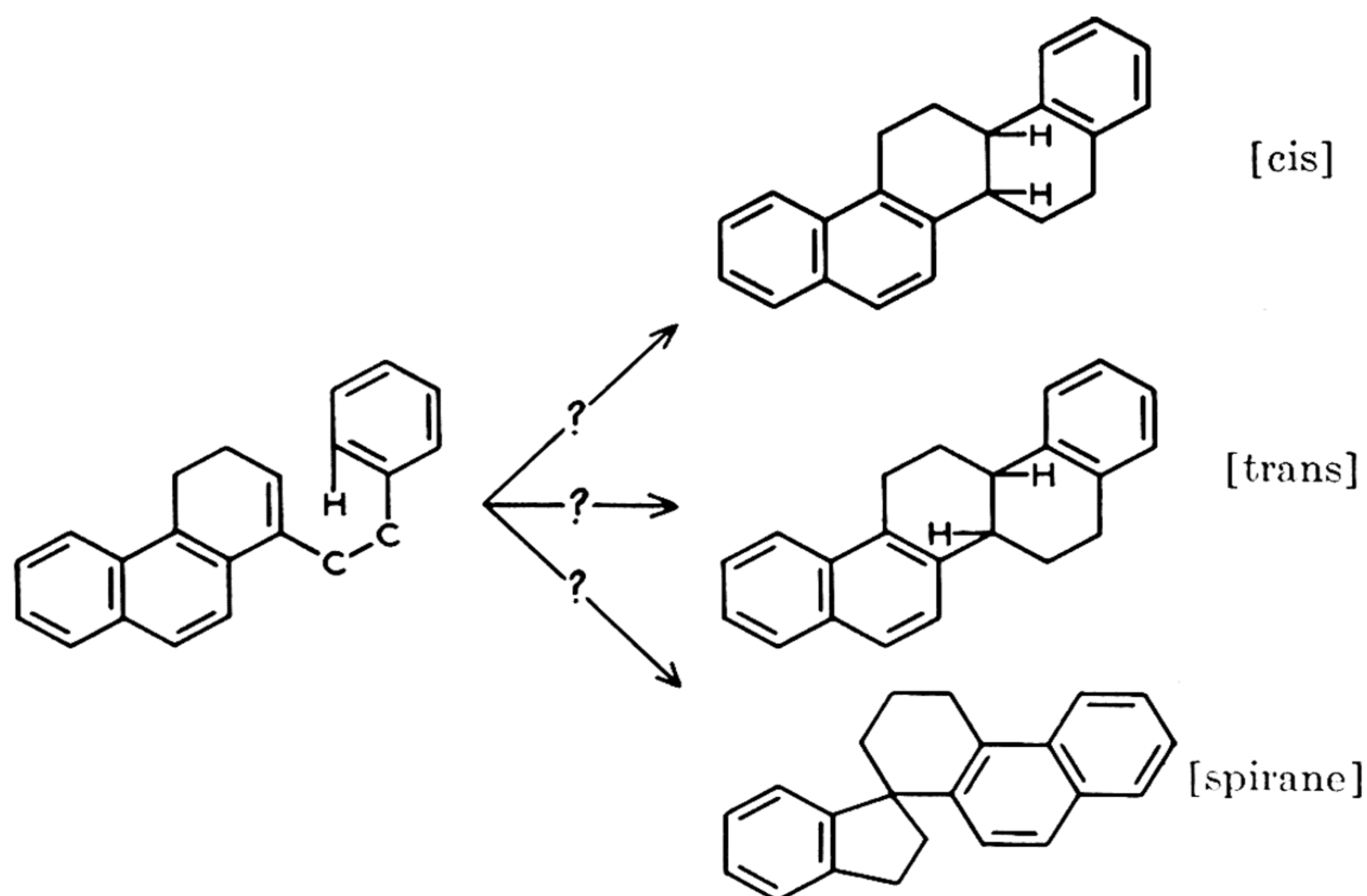
Treatment of 1-(β -phenethyl)-2-methyl-3- α -naphthindene with aluminum chloride plus carbon disulfide for 4 hours at 0° gave 60 per cent of 5,6,6a,13a-tetrahydro-13a-methyldibenzo[ag]fluorene (*i.e.*, methyltetrahydro-1,2,5,6-dibenzfluorene):¹¹³



A solution of 1,2-dihydro-4-(β -phenethyl)phenanthrene in carbon disulfide was treated with aluminum chloride for 12 hours at 0°, forming 61.5 per cent of 4b,5,6,12c,13,14-hexahydrobenzo[c]chrysene (*i.e.*, 3,4,4a,-9,10,10a-hexahydro-1,2,5,6-dibenzphenanthrene):⁴⁶

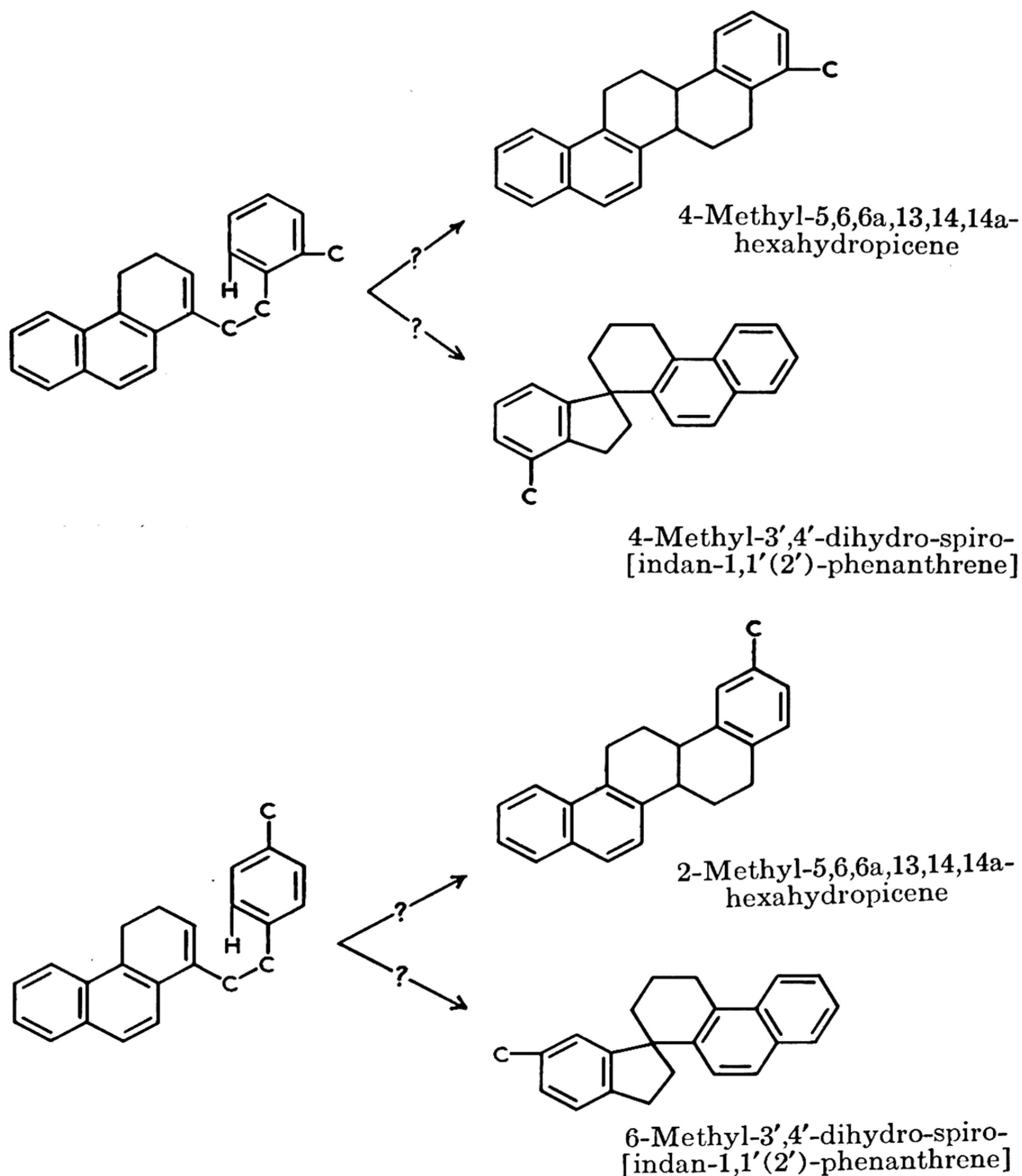


The action of aluminum chloride at 0-5° upon 1-(β -phenethyl)-3,4-dihydrophenanthrene (dissolved in carbon disulfide) probably gives a considerable amount of 3',4'-dihydro-spiro[indan-1,1'(2')-phenanthrene] and a small quantity of 5,6,6a,13,14,14a-hexahydropicene:¹⁴¹



Dehydrogenation of the product over a palladium-charcoal catalyst yielded much unchanged "spirane" and only one per cent of picene. The

cyclization of 1-(β -*o*-tolylethyl)-3,4-dihydrophenanthrene, and of 1-(β -*p*-tolylethyl)-3,4-dihydrophenanthrene, in the presence of aluminum chloride plus carbon disulfide has been described.¹⁴¹ The expected dehydrogenation products, 4-methylpicene and 2-methylpicene respectively, were not found after a heating of the cyclizates with a palladium-charcoal catalyst. The possible isomerizations can be formulated as follows:



The experimental data on aromatic-cyclene hydrocarbons, including calculated concentrations of catalysts and yields of products, are given in Table 42, p. 392.

Conclusions

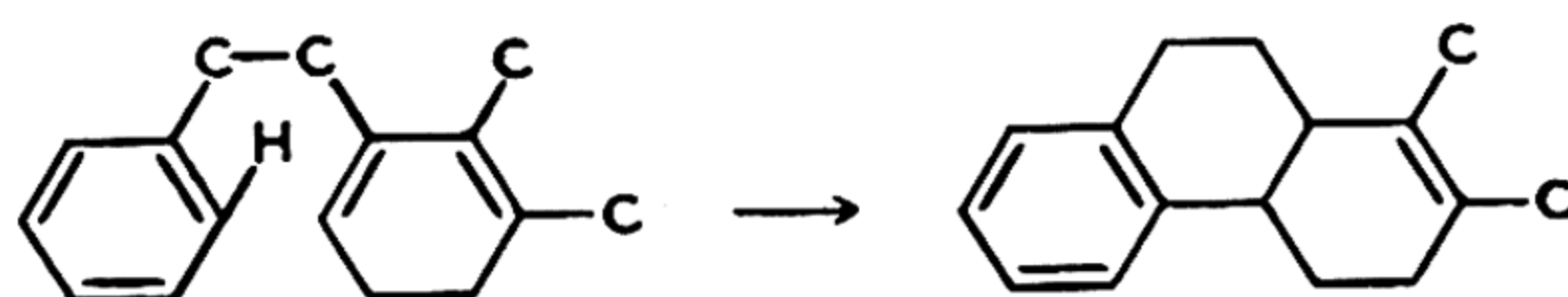
Aromatic cyclene hydrocarbons wherein a cyclene ring is attached to an aromatic ring (directly, or with one or two methylene groups in series

effecting the attachment) generally undergo cycloisomerization in the presence of such catalysts as: aluminum chloride plus carbon disulfide, stannic chloride plus hydrogen chloride and benzene, or sulfuric acid plus acetic acid.

AROMATIC-CYCLODIENE HYDROCARBONS

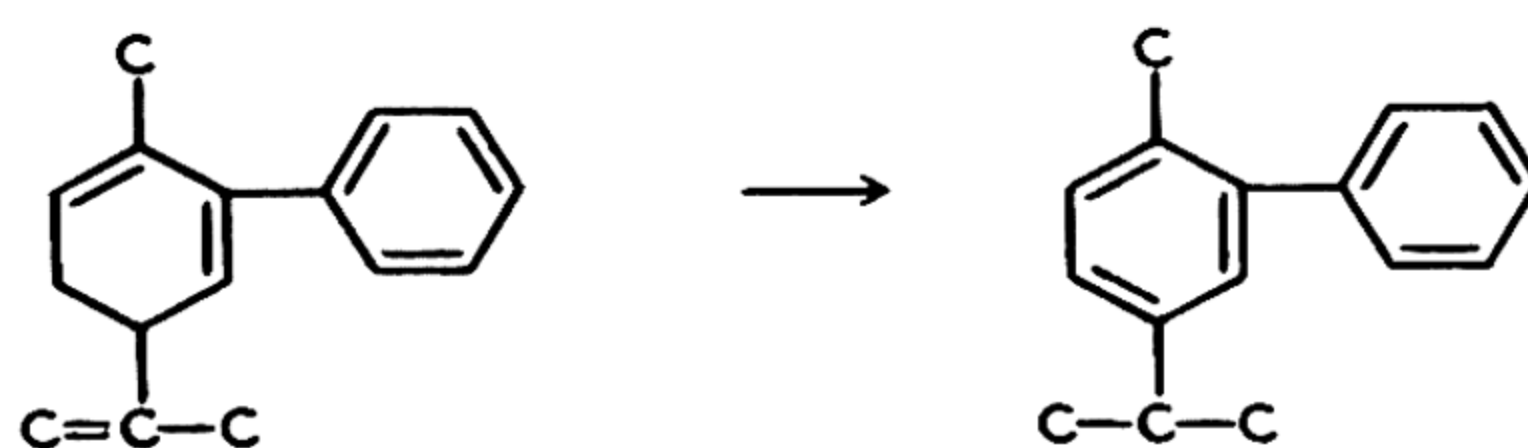
Isomerizations

Some aromatic-cyclodiene hydrocarbons can be expected to undergo cyclization in the manner of the foregoing aromatic-cyclenes. Unsaturated aliphatic side-chains apparently must be absent. 1,2-Dimethyl-3-(β -phenethyl)cyclohexadiene-1,3 was isomerized to 1,2-dimethyl-3,4,4a,-9,10,10a-hexahydrophenanthrene, *i.e.*, "1,2-dimethyl-3,4,9,10,11,12-hexahydrophenanthrene," by treatment with stannic chloride plus hydrogen chloride and benzene at 0°: ⁵⁶

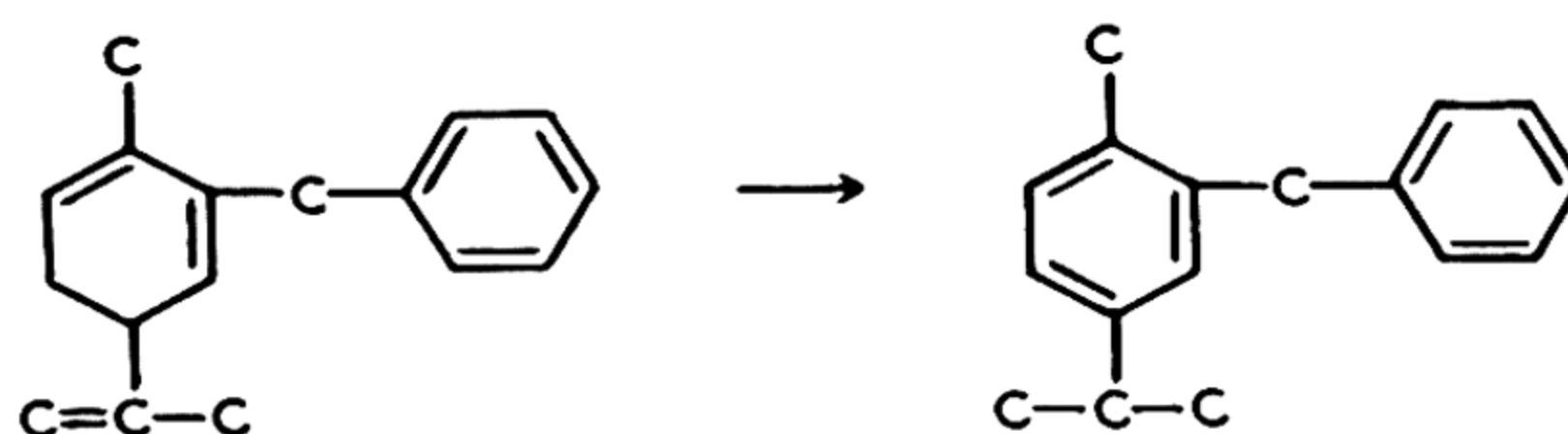


Aromatic-cyclodiene hydrocarbons undergo aromatization by double-bond migration rather than by cyclization when they contain an alkenyl group attached to the cyclodiene ring. The products formed in the known examples are polyalkyl biphenyl or polyalkyl diphenylmethane. As expected, acidic catalysts are used in these isomerizations.

1-Methyl-2-phenyl-4-isopropenylcyclohexadiene-2,6, heated under reflux for 5 hours with hydrogen chloride in acetic acid, gave 1-methyl-2-phenyl-4-isopropylbenzene: ³¹¹



"1-Methyl-2-benzyl-4-isopropenylcyclohexadiene-2,6" (which may be a mixture of 1-methyl-2-benzyl-4-isopropenyl-cyclohexadiene-3,6 and 1-methyl-2-benzal-4-isopropenyl-cyclohexene-6 ⁴⁸¹) undergoes an aromatization into 1-methyl-2-benzyl-4-isopropylbenzene. ^{310, 481} The catalyst is acetic acid containing one per cent of sulfuric acid: ⁴⁸¹



Summary

Isomerizations were discussed for individual members of the groups: alkanes, alkenes, allenic alkadienes, non-allenic alkadienes, alkapolyenes, alkynes, alkadiynes, alkapolyynes, cyclanes, cyclanes with saturated side-chains, cyclanes with unsaturated side-chains, spiranes, bicyclanes, bicyclanes with saturated side-chains, bicyclanes with unsaturated side-chains, tricyclanes, pentacyclanes, cyclenes, cyclenes with saturated side-chains, cyclenes with unsaturated side-chains, cyclodienes with saturated side-chains, cyclodienes with unsaturated side-chains, bicyclenes, bicyclenes with saturated side-chains, bicyclenes with unsaturated side-chains, bicyclodienes with saturated side-chains, tricyclenes, tricyclenes with saturated side-chains, tricyclenes with unsaturated side-chains, tetracyclenes, pentacyclenes, alkyl benzenes, alkenyl benzenes, allenic alkadienyl benzenes, non-allenic alkadienyl benzenes, alkapolyenyl benzenes, alkynyl benzenes, indanes, indenenes, fluorenes, naphthalenes, anthracenes, phenanthrenes, naphthacenes, aromatic-cyclane hydrocarbons, aromatic-cyclene hydrocarbons, and aromatic-cyclodiene hydrocarbons.

To enable the reader to make facile applications of the typical reactions that were "analyzed" in this survey, to other examples which he may encounter, it seems proper to give a few rules generally applicable in isomerization:

1. Isomerization tends to be a specific reaction. However, alkene isomerizations involving a change in branching generally develop some side products, because of the ease with which the branched alkenes are polymerized and depolymerized.

2. Isomerization has a tendency to produce a more compact structure of the molecule. Branched structures are the most compact and should have maximum stability. An equilibrium mixture of straight and branched molecules, especially, can be expected in the case of simpler structures.

3. In isomerization, systems having double bonds strive toward the attainment of conjugated positions.

4. The course of an isomerization is dependent on the reaction conditions (including catalyst effects). Sodium and sodamide generally convert an allenic alkadiene, alkyne-2, or alkyne-3 into the sodium derivative of an alkyne-1 (hydrolyzed by water to the free alkyne). Alcoholic alkalies and soda-lime convert an alkyne-1 into an allenic alkadiene or into an alkyne-2. Acidic reagents are effective catalysts

in isomerization via cyclization or via the shift of a double bond into an adjacent ring.

5. All isomerizations observed to date should proceed at least slightly in the reverse direction under proper reaction conditions. Specificity of mechanism alone does not prevent the reversibility in direction of an isomerization. In this respect, the directive action of sodium or sodamide is opposite in character to that of alcoholic alkalies or soda lime.

6. Isomerization involves changes in symmetry and saturation of molecules: (a) the *shifting* of alkyls, aryls, bicyclic bonds ("bridges"), and unsaturated bonds; (b) *contractions* and *expansions* of rings and side-chains; (c) *eliminations* and *formations* of rings, saturated or unsaturated side-chains, and of unsaturated bonds in general; and (d) the formation of geometrical (*cis-trans*) isomers.

7. Intercomparisons of the various groups of hydrocarbons indicate the prevalence of a fundamental allylic type or triad system of hydrogen migration. These comparisons should be an integral part of future experimental work on isomerization.

8. The specificity in formation of isomer products, as shown by their high yields in numerous cases, is probably the result of an advantageous change in the free energy of hydrocarbon molecules undergoing isomerization.

Last, but not least in importance, isomerization can be rigidly defined with respect to its several steps or changes in the molecule (Table 44), p. 400. The term "isomerization" should be used more specifically in the chemical literature, since the reaction is often accompanied (to a varying degree and with unknown significance) by "side reactions," such as alkylation, dealkylation, cracking, hydrogenation, dehydrogenation, or polymerization. The main reactions of alkylations, dehydration, hydration, oxidation, and reduction, in turn, can be accompanied by the formation of isomers. Therefore, a "true isomerization" or a "direct isomerization" is the formation of an isomer without the occurrence of a stable intermediate under specific reaction-conditions. "Delayed isomerization" is isomerization via stable intermediates, such as terpene hydrochlorides or the unsaturated ethers from the alkynes.

les of

Tables of

Tables of

Table

ation Datamerization Datamerization Datamerize

Table 6. Isomeriza					Table 6. Isomeriza					Table 6. Isomeriza				
Reactants					Reactants					Reactants				
Conc	Catal	Time	Temp	Alkane + catalyst	Conc	Catal	Time	Temp	Alkane + catalyst	Conc	Catal	Time	Temp	Alkane + catalyst
g			(°C)	n-Butane (100%)	g			(°C)	n-Butane (100%)	g			(°C)	n-Butane (100%)
1	n-Butane (100%)				1	n-Butane (100%)				1	n-Butane (100%)			
2 months	n-Butane (100%)				2 months	n-Butane (100%)				2 months	n-Butane (100%)			
620	n-Butane (100%)				620	n-Butane (100%)				620	n-Butane (100%)			
192	(100%)				192	(100%)				192	(100%)			
113	(124%)				113	(124%)				113	(124%)			
65	(134%)				65	(134%)				65	(134%)			
40	(233%)				40	(233%)				40	(233%)			
velocity)	(glass velocity)				velocity)	(glass velocity)				velocity)	(glass velocity)			
study)					study)					study)				
616	n-Butane (100%)				616	n-Butane (100%)				616	n-Butane (100%)			
193	n-Butane (100%)				193	n-Butane (100%)				193	n-Butane (100%)			
192	n-Butane (100%)				192	n-Butane (100%)				192	n-Butane (100%)			
114	n-Butane (100%)				114	n-Butane (100%)				114	n-Butane (100%)			
112	n-Butane (100%)				112	n-Butane (100%)				112	n-Butane (100%)			
64	n-Butane (100%)				64	n-Butane (100%)				64	n-Butane (100%)			
65.5	n-Butane (100%)				65.5	n-Butane (100%)				65.5	n-Butane (100%)			
40	n-Butane (100%)				40	n-Butane (100%)				40	n-Butane (100%)			
40	n-Butane (100%)				40	n-Butane (100%)				40	n-Butane (100%)			
24	88.4% (100%)				24	88.4% (100%)				24	88.4% (100%)			
11.8%	11.8% (100%)				11.8%	11.8% (100%)				11.8%	11.8% (100%)			
23	95% (100%)				23	95% (100%)				23	95% (100%)			
142	95% (100%)				142	95% (100%)				142	95% (100%)			
23	95% (100%)				23	95% (100%)				23	95% (100%)			
4	89% (100%)				4	89% (100%)				4	89% (100%)			
4	89% (100%)				4	89% (100%)				4	89% (100%)			
anhydrous)	n-Butane (100%) (anhydrous)				anhydrous)	n-Butane (100%) (anhydrous)				anhydrous)	n-Butane (100%) (anhydrous)			
	(513%)					(513%)					(513%)			
anhydrous)	n-Butane (100%) (anhydrous)				anhydrous)	n-Butane (100%) (anhydrous)				anhydrous)	n-Butane (100%) (anhydrous)			
hydrogen)	HCl (anhydrous)				hydrogen)	HCl (anhydrous)				hydrogen)	HCl (anhydrous)			
AlBr ₃	n-Butane (100%) or AlBr ₃				AlBr ₃	n-Butane (100%) or AlBr ₃				AlBr ₃	n-Butane (100%) or AlBr ₃			
hydrogen)	(anhydrous)				hydrogen)	(anhydrous)				hydrogen)	(anhydrous)			

一、资产		二、负债		三、所有者权益	
项目	金额	项目	金额	项目	金额
流动资产	1,000,000.00	流动负债	500,000.00	所有者权益	500,000.00
货币资金	100,000.00	短期借款	100,000.00	实收资本	500,000.00
应收账款	200,000.00	应付账款	100,000.00	资本公积	0.00
预付款项	50,000.00	预收账款	0.00	盈余公积	0.00
其他应收款	10,000.00	应付职工薪酬	10,000.00	未分配利润	0.00
存货	640,000.00	应交税费	90,000.00		
流动资产合计	1,000,000.00	流动负债合计	500,000.00	所有者权益合计	500,000.00
非流动资产	0.00	非流动负债	0.00		
固定资产	0.00	长期借款	0.00		
无形资产	0.00	应付债券	0.00		
其他非流动资产	0.00	其他非流动负债	0.00		
非流动资产合计	0.00	非流动负债合计	0.00		
资产合计	1,000,000.00	负债合计	500,000.00	所有者权益合计	500,000.00

[illegible]

Table 6. Isomeriza

Reactants		Catalyst (Per cent by weight on alkane + catalyst)	Contact Time (hours)	Temp. (°C.)
Alkane				
<i>n</i> -Butane		AlCl ₃ (anhydrous) HCl	380 cc. Butane and 38 cc. HCl per 9.1 g. catalyst per hour	130
<i>n</i> -Butane		AlCl ₃ (anhydrous) HCl	330 cc. Butane and 33 cc. HCl per 10.1 g. catalyst per hour	150
<i>n</i> -Butane		AlCl ₃ Carrier (pumice or silica)		below 160 (prefer- ably)
<i>n</i> -Butane		AlCl ₃ (16.4%) HCl (2% of input- <i>n</i> -butane) (1.6%)	12	150
<i>n</i> -Butane		AlCl ₃ (31.6%) HCl (8.3% of input- <i>n</i> -butane) (5.2%)	12	150
<i>n</i> -Butane		AlCl ₃ (anhydrous) (31.6%) HCl (anhydrous) (5.3%)	4	175
<i>n</i> -Butane		AlCl ₃ + activated carbon (1 : 1) HCl (2% of input-gas)	0.8 kgm. <i>n</i> -butane per kgm. catalyst per hour	200
<i>n</i> -Butane		AlCl ₃ + activated carbon (1 : 1) prepared with the aid of HCl at 250° and 25 atmospheres' H ₂ pressure HCl (2% of input-gas)	"moderate space ve- locity"	200
<i>n</i> -Butane		AlCl ₃ (anhydrous) (16.03%) CuSO ₄ · 2HCl (13.97%)	2.0	70
<i>n</i> -Butane Isobutane	89% 11%	AlCl ₃ Al ₂ O ₃ (prepared partially dehy- drated from Al(OH) ₃ at 300°) The catalyst had 84.5% of AlCl ₃ and 15.5% of Al ₂ O ₃ by weight.	0.12 kgm. feed per liter of catalyst per hour	100
<i>n</i> -Butane Isobutane	89% 11%	AlCl ₃ Al ₂ O ₃ (prepared partially dehy- drated from Al(OH) ₃ at 300°) The catalyst had 84.5% of AlCl ₃ and 15.5% of Al ₂ O ₃ by weight.	90 sec. or 0.063 kgm. feed per liter of catalyst per hour	120 130 140 150
<i>n</i> -Butane Isobutane	89% 11%	AlCl ₃ Al ₂ O ₃ (prepared partially dehy- drated from Al(OH) ₃ at 300°) The catalyst had about 84.5% of AlCl ₃ and about 15.5% of Al ₂ O ₃ by weight. HCl (5% by weight on input- butanes)	0.4 kgm. gases per liter of catalyst per hour	100
<i>n</i> -Butane Isobutane	91% 9%	AlCl ₃ Al ₂ O ₃ (prepared partially dehy- drated from Al(OH) ₃ at 300°)	30 g. feed per 250 cc. cata- lyst per hour	100

tion of Alkanes—Continued

Pressure (atms.)	Isobutane	Products (Per cent by weight on original alkane)		References
		Isomers	Other Products	
1 (?)	Isobutane	(37.2%)	CH ₄ <i>n</i> -Butane (0.06%) (62.7%)	(382)
1 (?)	Isobutane	(42.4%)	CH ₄ (?) C ₃ H ₈ <i>n</i> -Butane (33.55%) (24.1%)	(382)
(gas phase)	Isobutane			(416b)
30	Isobutane	(66.5%)	<i>n</i> -Butane (31.9%)	(604) (605)
30	Isobutane	(13.3%)	CH ₄ C ₂ H ₆ C ₃ H ₈ Liquid hydrocarbons (4.5%) (7.6%) (42.0%) (20.0%)	(604)
35	Isobutane	(13.3%)	H ₂ CH ₄ C ₂ H ₆ C ₃ H ₈ <i>n</i> -Butane Heavy brown oil (0.07%) (4.5%) (7.7%) (42%) (10%) (20%)	(276)
44	Isobutane	(53%)	C ₃ H ₈ <i>n</i> -Butane Liquid hydrocarbons (3%) (36%) (8%)	(604)
44	Isobutane	(53%)	C ₃ H ₈ <i>n</i> -Butane Liquid hydrocarbons (3%) (36%) (8%)	(284)
sealed tube (liquid phase)	Isobutane	(48.3%)	<i>n</i> -Butane (51.7%)	(382)
11	Isobutane	(55%)	<i>n</i> -Butane (45%)	(165a)
1	Isobutane	(38%)		(165a)
1	Isobutane	(38%)		
1	Isobutane	(43%)		
1	Isobutane (Shows temperature effect)	(50%)		
11	Isobutane	(58%)	<i>n</i> -Butane	(165a)
11	Isobutane (first 44 hours) Isobutane (succeeding 56 hours)	(50%) (65–57%)		(165a)

Table 6. Isomeriza

Alkane	Reactants		Contact Time (hours)	Temp. (°C.)
		Catalyst (Per cent by weight on alkane + catalyst) The catalyst had 87% of AlCl_3 and 13% of Al_2O_3 by weight. HCl (5% by weight on input- butanes and only after 44 hours' run)		
<i>n</i> -Butane Isobutane	89% 11%	AlCl_3 Pipe clay (partially dehydrated at 300° for 2 hours)	during first 44 hours 60–100 g. feed per 250 cc. catalyst per hour during the succeed- ing 56 hours	about 100
<i>n</i> -Butane Isobutane	89% 11%	AlCl_3 Pipe clay (partially dehydrated at 300°) The catalyst had 71.2% of AlCl_3 and 28.8% of pipe clay by weight.	0.13 kgm. feed per liter of catalyst per hour	120
<i>n</i> -Butane Isobutane	88.5% 11.5%	AlCl_3 (sublimed) Powdered pipe clay (partially dehydrated at 300°) The catalyst had 71.5% of AlCl_3 and 28.5% of pipe clay by weight.	93 sec. (one pass)	150
<i>n</i> -Butane Isobutane	88.5% 11.5%	AlCl_3 (sublimed) Powdered pipe clay (completely dehydrated at 1100°)	(one pass)	150
<i>n</i> -Butane Isobutane	88.5% 11.5%	AlCl_3 (sublimed) Kaolinite (dehydrated at 300°) The catalyst had 74.8% of AlCl_3 and 29.8% of kaolinite by weight.	93 sec.	150
<i>n</i> -Butane Isobutane	88.5% 11.5%	AlCl_3 (sublimed) Kaolinite (dehydrated at 1100°) The catalyst had 74.8% of AlCl_3 and 29.8% of kaolinite by weight.	93 sec.	150
<i>n</i> -Butane Isobutane	88.1% 11.9%	AlCl_3 Pumice The catalyst had 22.5% of AlCl_3 and 77.5% of pumice by weight.	20 sec.	150
<i>n</i> -Butane Isobutane	91% 9%	AlCl_3 Al_2O_3 (prepared partially dehy- drated from $\text{Al}(\text{OH})_3$ at 300°) Powdered pumice (previously de- hydrated at 500°) The catalyst had 44 g. AlCl_3 , 20 g. Al_2O_3 , and 13 g. pumice.	2.5 liters feed per 77 g. catalyst per hour (one pass)	150
<i>n</i> -Butane Isobutane	91% 9%	AlCl_3 Silica gel (dehydrated at 300°) Pumice (dehydrated at 300°) The catalyst had 37 g. AlCl_3 , 24.5 g. silica gel, and 8.5 g. pumice.	2.5 liters feed per 70 g. catalyst per hour (one pass) (one pass)	150
<i>n</i> -Butane Isobutane	91% 9%	AlCl_3 Silica gel (dehydrated at 1100°) Pumice (dehydrated at 300°)	(one pass)	150
<i>n</i> -Butane Isobutane	91% 9%	AlCl_3 Sodium permutite (dehydrated at 110°) The catalyst had 53 g. AlCl_3 and 29 g. sodium permutite.	2.5 liters feed per 82 g. catalyst per hour (one pass)	150

tion of Alkanes—Continued

Pressure (atms.)	Isomers	Products (Per cent by weight on original alkane)		Refer- ences
		Isomers	Other Products	
about 11	Isobutane	(55%?)	<i>n</i> -Butane (45%?)	(165a)
11	Isobutane	(61.4%)	<i>n</i> -Butane (37.7%) Decomposition products (0.9%)	(165a)
1	Isobutane	(54%)	<i>n</i> -Butane (46%)	(165a)
1	Isobutane	(14.5%)		(165a)
1	Isobutane	(54%)	<i>n</i> -Butane (46%)	(420c)
1	Isobutane	(26%)	<i>n</i> -Butane (74%)	(420c)
(gas phase)	Isobutane	(28%)	<i>n</i> -Butane (72%)	(420b)
1	Isobutane	(42%)		(165a)
1	Isobutane	(33%)		(165a)
1	Isobutane	(1.7%)		(165a)
1	Isobutane	(20.2%)		(165a)

Table 6. Isomeriza

Alkane	Reactants		Catalyst (Per cent by weight on alkane+catalyst)	Contact Time (hours) (one pass)	Temp. (°C.)
<i>n</i> -Butane Isobutane	91% 9%	AlCl ₃ Sodium permutite (dehydrated at 1100°)			150
<i>n</i> -Butane Isobutane	89% 11%	AlCl ₃ HCl	(31.2%) (6.3%)	4	20
<i>n</i> -Butane Isobutane	89% 11%	AlCl ₃ HCl	(31.2%) (6.3%)	4	40
<i>n</i> -Butane Isobutane	89% 11%	AlCl ₃ HCl	(31.2%) (6.3%)	4	60
<i>n</i> -Butane Isobutane	38% 62%	AlCl ₃ HCl			60
<i>n</i> -Butane Isobutane	24.9% 75.1%	AlCl ₃ HCl			60
<i>n</i> -Butane Isobutane	40.4% 57.4%	AlCl ₃ HCl			60
<i>n</i> -Butane Isobutane	38.6% 58.2%	AlCl ₃ HCl			60
<i>n</i> -Butane Isobutane	89% 11%	AlCl ₃ HCl	(31.2%) (6.3%)	4	80
<i>n</i> -Butane Isobutane	89% 11%	AlCl ₃ HCl	(31.2%) (6.3%)	4	100
<i>n</i> -Butane Isobutane	90% 10%	AlCl ₃ on a carrier HCl (6% by weight of butanes)		200 g. butanes per 250 cc. solid cata- lyst per hour	100
<i>n</i> -Butane and Isobutane mixtures		AlCl ₃ on a carrier HCl (2 mole % on butanes)		(flow experi- ments)	100
<i>n</i> -Butane Isobutane	41.4% 58.2%	AlCl ₃ HCl			100
<i>n</i> -Butane Isobutane	39.3% 60.5%	AlCl ₃ HCl			100
<i>n</i> -Butane Isobutane	32.0% 68.0%	AlCl ₃ HCl			100
<i>n</i> -Butane Isobutane	19.4% 80.6%	AlCl ₃ HCl			100
<i>n</i> -Butane Isobutane	89% 11%	AlCl ₃ HCl	(31.2%) (6.3%)		120
<i>n</i> -Butane Isobutane	38% 62%	AlCl ₃ HCl	(trace)		140

tion of Alkanes—Continued

Pressure (atms.) 1	Products (Per cent by weight on original alkane)			Refer- ences (165a)
	Isomers	Isobutane	Other Products	
		(5%)		
autoclave	Isobutane	(15.0%)	<i>n</i> -Butane (85.0%)	(529a)
autoclave	Isobutane	(17.6%)	<i>n</i> -Butane (82.4%)	(529a)
autoclave	Isobutane	(22.6%)	<i>n</i> -Butane (77.8%)	(529a)
autoclave (liquid phase)	Isobutane Isobutane $\frac{\text{Isobutane}}{\text{Isobutane}} = 1.82$	(64.1%)	<i>n</i> -Butane (35.3%) Side products (0.6%)	(529a)
autoclave (liquid phase)	<i>n</i> -Butane Isobutane $\frac{\text{Isobutane}}{\text{Isobutane}} = 2.16$	(31.4%)	Isobutane (67.9%) Side products (0.7%)	(529a)
autoclave (liquid phase)	Isobutane Isobutane $\frac{\text{Isobutane}}{\text{Isobutane}} = 2.09$	(64.7%)	<i>n</i> -Butane (31.0%) Side products (4.3%)	(529a)
autoclave (liquid phase)	Isobutane Isobutane $\frac{\text{Isobutane}}{\text{Isobutane}} = 2.03$	(62.8%)	<i>n</i> -Butane (31.9%) Side products (5.3%)	(529a)
autoclave	Isobutane "Equilibrium conditions"	(35.1%)	<i>n</i> -Butane (64.9%)	(529a)
autoclave	Isobutane	(62.9%)	Propane (3.8%) <i>n</i> -Butane (29.4%) Pentanes and higher (3.9%)	(529a)
16 (gas phase)	Isobutane (12–24 hour period) (66.4%) (60–72 hour period) (63.6%) (120–132 hour period) (60.8%)		<i>n</i> -Butane (28.1%) (12–24 hour period) (32.7%) (60–72 hour period) (36.0%) (120–132 hour period) (36.0%) Side products (12–24 hour period) (5.5%) (60–72 hour period) (3.7%) (120–132 hour period) (3.2%)	(529a)
11 (gas phase)	Isobutane (from isobutane side) (65.0%) (from <i>n</i> -butane side) (65.3%) "Equilibrium conditions"		<i>n</i> -Butane (25.8%) (from isobutane side) (26.1%) Side products (from isobutane side) (9.2%) (from <i>n</i> -butane side) (8.6%)	(135a)
autoclave (liquid phase)	Isobutane Isobutane $\frac{\text{Isobutane}}{\text{Isobutane}} = 2.05$	(64.3%)	<i>n</i> -Butane (31.5%) Side products (4.2%)	(529a)
autoclave (liquid phase)	Isobutane Isobutane $\frac{\text{Isobutane}}{\text{Isobutane}} = 2.23$	(66.4%)	<i>n</i> -Butane (29.8%) Side products (3.8%)	(529a)
autoclave (liquid phase)	Isobutane <i>n</i> -Butane $\frac{\text{Isobutane}}{\text{Isobutane}} = 2.05$		<i>n</i> -Butane (30.9%) Isobutane (65.5%) Side products (3.6%)	(529a)
autoclave (liquid phase)	<i>n</i> -Butane Isobutane $\frac{\text{Isobutane}}{\text{Isobutane}} = 2.48$	(27.7%)	Isobutane (68.5%) Side products (3.8%)	(529a)
autoclave	Isobutane	(16.7%)	Propane (70.5%) <i>n</i> -Butane (10.0%) Pentanes and higher (2.8%)	(529a)
5 (H ₂) (gas phase?)	Isobutane <i>n</i> -Butane $\frac{\text{Isobutane}}{\text{Isobutane}} = 1.65$		<i>n</i> -Butane (37.2%) Isobutane (61.5%) Side products (1.3%)	(529a)

Table 6. Isomeriza

Alkane	Reactants		Catalyst (Per cent by weight on alkane + catalyst)	Contact Time (hours)	Temp. (°C.)
<i>n</i> -Butane	24.9%	AlCl ₃			140
Isobutane	75.1%	HCl	(trace)		
<i>n</i> -Butane	40.4%	AlCl ₃			140
Isobutane	57.4%	HCl	(trace)		
<i>n</i> -Butane	38.6%	AlCl ₃			140
Isobutane	58.2%	HCl	(trace)		
<i>n</i> -Butane	89%	AlCl ₃	(33%)	16	20
Isobutane	11%	HCl		2	70
				18	70
				4	100
<i>n</i> -Butane	89%	AlCl ₃	(31.1%)	4	20
Isobutane	11%	HCl (anhydrous)	(5.9%)		
<i>n</i> -Butane	89%	AlCl ₃	(31.1%)	16	20
Isobutane	11%	HCl (anhydrous)	(5.9%)		
<i>n</i> -Butane	89%	AlCl ₃	(24.4%)	16	20
Isobutane	11%	HCl (anhydrous)	(26.3%)		
<i>n</i> -Butane	89%	AlCl ₃	(31.1%)	64	20
Isobutane	11%	HCl (anhydrous)	(5.9%)		
<i>n</i> -Butane	89%	AlCl ₃	(31.1%)	16	65
Isobutane	11%	HCl (anhydrous)	(5.9%)		
<i>n</i> -Butane	89%	AlCl ₃	(31.1%)	4	80
Isobutane	11%	HCl (anhydrous)	(5.9%)		
<i>n</i> -Butane	89%	AlCl ₃	(31.1%)	5	90
Isobutane	11%	HCl (anhydrous)	(5.9%)		
<i>n</i> -Butane	89%	AlCl ₃	(31.1%)	4	100
Isobutane	11%	HCl (anhydrous)	(5.9%)		
<i>n</i> -Butane	89%	AlCl ₃	(31.1%)	4	120
Isobutane	11%	HCl (anhydrous)	(5.9%)		
<i>n</i> -Butane and Isobutane mixtures		AlBr ₃ (?) or AlCl ₃ (?)		1000 or more	10
		AlBr ₃ (?) or AlCl ₃ (?)			20
		AlBr ₃ (?) or AlCl ₃ (?)			52
		AlBr ₃ (?) or AlCl ₃ (?)			99
		AlCl ₃			123
		AlCl ₃			150
<i>n</i> -Butane and Isobutane mixtures		AlCl ₃ + CuSO ₄ · 2HCl			70
<i>n</i> -Butane and Isobutane mixtures		AlCl ₃ HCl (part of input-gas)			110
<i>n</i> -Butane and Isobutane mixtures		AlCl ₃ HCl (part of input-gas)			130

tion of Alkanes—Continued

Pressure (atms.)	Products (Per cent by weight on original alkane)			Refer- ences
	Isomers	Other Products		
5 (H ₂) (gas phase?)	$\frac{n\text{-Butane}}{\text{Isobutane}} = 2.29$	(29.8%) Isobutane Side products	(68.3%) (1.9%)	(529a)
5 (H ₂) (gas phase?)	$\frac{n\text{-Butane}}{\text{Isobutane}} = 1.53$	(58.1%) <i>n</i> -Butane Side products	(38.1%) (3.8%)	(529a)
5 (H ₂) (gas phase?)	$\frac{n\text{-Butane}}{\text{Isobutane}} = 1.82$	(58.5%) <i>n</i> -Butane Side products	(32.2%) (9.3%)	(529a)
20 of HCl 4 of HCl 4 of HCl 4 of HCl (all liquid phase)	<i>n</i> -Butane "Equilibrium conditions" Isobutane Isobutane Isobutane Isobutane (yield study or disclosure)	(22.3%) (23.5%) (51%) (62.9%)		(420d)
3-4 of HCl (liquid phase)	Isobutane (15.0% in reaction mixture)			(418)
4 of HCl (liquid phase)	Isobutane (16.8% in reaction mixture)			(418)
20 of HCl (liquid phase)	Isobutane (22.3% in reaction mixture)			(418)
4 of HCl (liquid phase)	Isobutane (21.3% in reaction mixture)			(418)
4 of HCl (liquid phase)	Isobutane (51.2% in reaction mixture)			(418)
4 of HCl (liquid phase)	Isobutane (35.0% in reaction mixture)			(418)
4 of HCl (liquid phase)	Isobutane (65.0% in reaction mixture)	Non-C ₄ hydrocarbons	(1-2%)	(418)
4 of HCl (liquid phase)	Isobutane (62.9% in reaction mixture)	Non-C ₄ hydrocarbons	(7.7%)	(418)
4 of HCl (liquid phase)	Isobutane (16.7% in reaction mixture)	Non-C ₄ hydrocarbons	(73.3%)	(418)
vapor phase 1 (?)	$\frac{\text{Isobutane}}{n\text{-Butane}} = 7.33$			(366)
vapor phase	$\frac{\text{Isobutane}}{n\text{-Butane}} = 5.06$			
vapor phase	$\frac{\text{Isobutane}}{n\text{-Butane}} = 4.21$			
vapor phase	$\frac{\text{Isobutane}}{n\text{-Butane}} = 3.00$			
vapor phase	$\frac{\text{Isobutane}}{n\text{-Butane}} = 2.33$	Propane		
vapor phase	$\frac{\text{Isobutane}}{n\text{-Butane}} = 1.86$	Propane		
sealed tube (liquid phase)	"Equilibrium conditions" in all 6 cases $\frac{\text{Isobutane}}{n\text{-Butane}} = 3.8$ (by equation; ex- periments show 2.8) "Equilibrium conditions"			(382)
1 (?)	$\frac{\text{Isobutane}}{n\text{-Butane}} = 2.6$			(382)
1 (?)	"Equilibrium conditions" $\frac{\text{Isobutane}}{n\text{-Butane}} = 2.0$ "Equilibrium conditions"	Propane ("especially when work- ing with isobutane")		(382)

Table 6. Isomeriza

Reactants		Catalyst (Per cent by weight on alkane + catalyst)	Contact Time (hours)	Temp. (°C.)
Alkane				
<i>n</i> -Butane and Isobutane mixtures		AlCl ₃ HCl (part of input-gas)		150
<i>n</i> -Butane and Isobutane mixtures		AlCl ₃ + KCl + ground glass HCl (part of input-gas)		180
Isobutane		AlBr ₃ (18.9%)	2 months	27
Isobutane		AlCl ₃ (anhydrous) HCl	320 cc. isobu- tane and 38 cc. HCl per 9.0 g. cata- lyst per hour	130
Isobutane		AlCl ₃ (anhydrous) HCl	340 cc. isobu- tane and 34 cc. HCl per 10.5 g. cata- lyst per hour	150
Isobutane		AlCl ₃ (anhydrous) KCl Ground glass (diluent) HCl	350 cc. isobu- tane and 35 cc. HCl per 38.3 g. AlCl ₃ and 5.7 g. KCl (<i>i.e.</i> , 44 g. catalyst) per hour	180
Isobutane		AlCl ₃ (anhydrous) CuSO ₄ · 2HCl	(16.03%) (13.97%) 2.5	70
<i>n</i> -Pentane		AlBr ₃ (7.1%)	504	0
<i>n</i> -Pentane		AlBr ₃ (7.1%)	168	27
<i>n</i> -Pentane Isopentane	80.0% 20.0%	AlBr ₃ (7.1%)	68	27
<i>n</i> -Pentane Isopentane	68.9% 31.1%	AlBr ₃ (7.1%)	68	27
<i>n</i> -Pentane Isopentane	60.0% 40.0%	AlBr ₃ (7.1%)	68	27
<i>n</i> -Pentane		AlBr ₃ (anhydrous) (9.7%)	95	room
<i>n</i> -Pentane <i>n</i> -Pentane		AlCl ₃ (freshly sublimed) AlCl ₃ (freshly sublimed)	several days	b. p. 40–133
<i>n</i> -Pentane		AlCl ₃ (22.9–28.3%) H ₂ O (0.6–0.8%)	5–10 days	b. p.
<i>n</i> -Pentane		AlCl ₃ (lump or powder) (33.3%)	20	23.9
<i>n</i> -Pentane		AlCl ₃ (32.9%) H ₂ O (1.3%)	20	23.9
<i>n</i> -Pentane		AlCl ₃ (8.9%) HCl (1.8%)	20	23.9
<i>n</i> -Pentane		AlCl ₃ (32.9%) HCl (1.3%)	20	23.9

Reaction of Alkynes—Continued

[illegible]

Table 6. Isomeriza

Alkane	Reactants		Contact Time (hours)	Temp. (°C.) b. p.	
	Catalyst (Per cent by weight on alkane + catalyst)				
<i>n</i> -Pentane	AlCl ₃ with any of the following: HBr (anhydrous) HCl (anhydrous) AlCl ₃ (hydrated) Alkyl chlorides				
<i>n</i> -Pentane	AlCl ₃ with either: HBr (anhydrous) (2.5%) H ₂ O (2.5%)				40
<i>n</i> -Pentane	AlCl ₃ (5–10% by weight of <i>n</i> -pentane) HCl (0.1–1% by weight of <i>n</i> -pentane)		4–5 days or 0.5 hour	at at	room 200
<i>n</i> -Pentane	AlCl ₃ on inert carriers such as: Activated carbon Silica Fuller's earth Fire-brick HCl (below 2% by weight of <i>n</i> -pentane)		continuous operation		room- 200
<i>n</i> -Pentane	AlCl ₃ (45%) HCl (9.9%)		3		room
<i>n</i> -Pentane	AlCl ₃ (about 45%) HCl (about 9.9%)		about 2		about 26
<i>n</i> -Pentane	AlCl ₃ (anhydrous) (9.0%) HCl (gas) (0.9%)		3		100
<i>n</i> -Pentane	50% AlCl ₃ + 50% activated carbon base HCl (1% of input-gas)		1	part <i>n</i> -pentane per 1.2 parts by weight of AlCl ₃ + active carbon per hour	200
<i>n</i> -Pentane	AlCl ₃ on activated carbon HCl (1% of input-gas)			continuous operation	200
<i>n</i> -Pentane	AlCl ₃ (44.6%) HCl (9.8%) ClSO ₃ H (1.0%)		2		26
<i>n</i> -Pentane	AlCl ₃ (44.6%) HCl (9.8%) FSO ₃ H (0.9%)		3		room
<i>n</i> -Pentane	AlCl ₃ (43.1%) HCl (9.5%) FSO ₃ H (4.3%)		about 3		room
<i>n</i> -Pentane	AlCl ₃ (8.8%) BF ₃ (below 2.7%)		20		23.9
<i>n</i> -Pentane	AlCl ₃ (32.7%) BF ₃ (below 1.9%)		20		23.9
<i>n</i> -Pentane	2AlCl ₃ . 1BF ₃ (yellow complex) (9.1%)		20		26.7
<i>n</i> -Pentane	AlCl ₃ (8.33%) CuSO ₄ . 2HCl (8.33%)		4.5		50
<i>n</i> -Pentane	2AlCl ₃ . 1C ₆ H ₅ (<i>tert</i> -C ₄ H ₉) (this liquid complex contains 66% of combined AlCl ₃ , 40 cc. were used for 100 g. of pentane feed)		2.5 and 18	at at	35 120

tion of Alkanes—Continued

Pressure (atms.)	Isomers	Products (Per cent by weight on original alkane)			Refer- ences (216)
		Isomers	Other Products	Other Products	
1	Isopentane	(large %)	Butanes Saturated higher-boiling prod- ucts Insoluble unsaturated polymer		
1 (N ₂)	Isopentane	(about 13.4%)	H ₂ (traces) n-Butane (about 3%) Isobutane (about 30%) Higher-boiling products		(216)
over 10	Isopentane	(60% per cycle) (90% with recycle)			(603)
over 10	Isopentane				(603)
13.6–14.3 (HCl)	Isopentane	(60%)	n-Pentane	(9%)	(357a)
HCl	Isopentane	(about 66%)	n-Pentane	(26%)	(357a)
5 (measured at 20°)	Isopentane	(30%)	Isobutane (30%) n-Pentane (30%) Higher hydrocarbons (10%)		(603)
30	Isopentane	(27% per pass) (80% with recycle)	n-Butane (3.5% by vol.) Isobutane (3.5% by vol.)		(603)
30	Isopentane	(27% per pass) (80% with recycle)			(605)
13.6–14.3 (HCl)	Isopentane	(65%)	C ₄ and C ₆ hydrocarbons (3%) n-Pentane (32%)		(357a)
13.6–14.3 (HCl)	Isopentane	(81%)	C ₄ , C ₆ , and heavier hydrocarbons (small %) n-Pentane (9%)		(357a)
13.6–14.3 (HCl)	Isopentane	(62%)	n-Pentane (5%)		(357a)
autoclave	Isopentane	(26%)	"Butane" (2%)		(37a)
autoclave	Isopentane	(70%)	"Butane" (2%)		(37a)
autoclave	Isopentane	(40%)	"Butane" (12%)		(37a)
sealed tube (liquid phase)	Isopentane Isopentane n-Pentane = 4.40	(21.7%)	n-Butane (7.5%) Isobutane (27%) n-Pentane (4.93%) High-boiling fraction (26%)		(382a)
1 (?)	Isopentane	(18.3%)	Isobutane (8.7%) n-Pentane (73.0%)		(420a)

Table 6. Isomeriza

Reactants		Catalyst (Per cent by weight on alkane+catalyst)	Contact Time (hours)	Temp. (°C.)
Alkane				
<i>n</i> -Pentane		2AlCl ₃ . 1C ₆ H ₅ (<i>tert</i> -C ₄ H ₉) (30 cc. of this liquid complex were used for 100 g. of pentane feed) AlCl ₃ (also used, 30 g. for 100 g. of pentane feed)	120	120
<i>n</i> -Pentane		ZrCl ₄ (anhydrous) (22.4%) HCl (gas)	3	150
Isopentane		AlBr ₃ (7.1%)	504	0
Isopentane	90.0%}	AlBr ₃ (7.1%)	240	0
<i>n</i> -Pentane	10.0%}			
Isopentane	85.0%}	AlBr ₃ (7.1%)	240	0
<i>n</i> -Pentane	15.0%}			
Isopentane		AlBr ₃ (9.09%)	19 days	25
Isopentane	70%}	AlBr ₃ (9.09%)	55 days	25
<i>n</i> -Pentane	30%}			
Isopentane		AlBr ₃ (7.1%)	168	27
Isopentane	70.8%}	AlBr ₃ (7.1%)	68	27
<i>n</i> -Pentane	29.2%}			
Isopentane	60.8%}	AlBr ₃ (7.1%)	68	27
<i>n</i> -Pentane	39.2%}			
Isopentane	70%}	AlCl ₃ (9.09%)	4.0	70
<i>n</i> -Pentane	30%}	HCl (anhydrous) (?%)		
Isopentane	85%}	AlCl ₃ (9.09%)	4.0	70
<i>n</i> -Pentane	15%}	HCl (anhydrous) (?%)		
Isopentane	95.5%}	AlCl ₃ (8.33%)	24	80
<i>n</i> -Pentane	4.1%}	HCl (8.33%)		
Isopentane	87.5%}	AlCl ₃ (8.33%)	24	80
<i>n</i> -Pentane	12.0%}	HCl (8.33%)		
Isopentane	79.7%}	AlCl ₃ (8.33%)	24	80
<i>n</i> -Pentane	19.9%}	HCl (8.33%)		
Isopentane	68%}	AlCl ₃ (9.09%)	2.5	90
<i>n</i> -Pentane	32%}	HCl (anhydrous) (?%)		
Isopentane		AlCl ₃ (8.33%)	4.5	50
		CuSO ₄ . 2HCl (8.33%)		

Reaction of Alkanes—Continued

[illegible]

Table 6. Isomeriza

Reactants		Catalyst (Per cent by weight on alkane + catalyst)	Contact Time (hours)	Temp. (°C.)
Alkane				
Isopentane		AlCl ₃ (8.33%) CuSO ₄ · 2HCl (8.33%)	1.3	90
Isopentane	70% }	AlCl ₃ (8.33%)	1.5	90
<i>n</i> -Pentane	30% }	CuSO ₄ · 2HCl (8.33%)		
Isopentane	80% }	AlCl ₃ (8.33%)	1.5	90
<i>n</i> -Pentane	20% }	CuSO ₄ · 2HCl (8.33%)		
Tetramethylmethane		AlBr ₃ (16.3–29.1%)	2300	room
<i>n</i> -Hexane		Cu tube	25 sec.	609
<i>n</i> -Hexane		Glass tube	6	420
<i>n</i> -Hexane		Glass tube	1	450
<i>n</i> -Hexane		SiO ₂ (10%)	100	370
<i>n</i> -Hexane		Glass tube		
<i>n</i> -Hexane		SiO ₂ (10%)	6	420
<i>n</i> -Hexane		Glass tube		
<i>n</i> -Hexane		MoS ₂ (10%)	6	420
<i>n</i> -Hexane		Glass tube		
<i>n</i> -Hexane		MoS ₂ (20%)	2	400
<i>n</i> -Hexane		Steel autoclave		
<i>n</i> -Hexane		AlBr ₃ (5.9–8.7%)		room
<i>n</i> -Hexane		AlCl ₃ (3%)	1.5	77–80
<i>n</i> -Hexane		Propyl bromide		
<i>n</i> -Hexane		AlCl ₃ (3%)	3	77–80
<i>n</i> -Hexane		Propyl bromide		
<i>n</i> -Hexane		AlCl ₃ (5%)	1.5	80
<i>n</i> -Hexane		AlCl ₃ (5%)	1	90
<i>n</i> -Hexane		AlCl ₃ (4%)	2	90
<i>n</i> -Hexane		AlCl ₃ (4%)	3	90
<i>n</i> -Hexane		AlCl ₃ (5%)	1	90
<i>n</i> -Hexane		Propyl chloride (3%)		
<i>n</i> -Hexane		AlCl ₃ (5%)	2	90
<i>n</i> -Hexane		Propyl chloride (3%)		
<i>n</i> -Hexane		AlCl ₃ (5%)	1	45
<i>n</i> -Hexane		Propyl chloride (3%)		
<i>n</i> -Hexane		AlCl ₃ (5%)	3	45
<i>n</i> -Hexane		Propyl chloride (3%)		
<i>n</i> -Hexane		AlCl ₃ (9.09%)	2 (?)	40
<i>n</i> -Hexane		AlCl ₃ (9.09%)	2	80
<i>n</i> -Hexane		AlCl ₃ (9.09%)	2 (?)	100
<i>n</i> -Hexane		AlCl ₃ (9.09%)	2 (?)	120
<i>n</i> -Hexane		AlCl ₃ (27.0%)	7.5	68–100
<i>n</i> -Hexane		H ₂ O (1.0%)		
<i>n</i> -Hexane		AlCl ₃ (9.0%)	3	69–72
<i>n</i> -Hexane		HCl (1.0%)		
<i>n</i> -Hexane		AlCl ₃	16	80
2-Methylpentane		HCl		
2-Methylpentane		AlBr ₃ (5.9–8.7%)		room
2-Methylpentane		AlCl ₃	16	80
2-Methylpentane		HCl		
2-Methylpentane		(96%) H ₂ SO ₄ + (4%) H ₂ O	500	

[illegible]

Table 6. Isomeriza

Alkane	Reactants	Catalyst (Per cent by weight on alkane + catalyst)	Contact Time (hours)	Temp. (°C.)
3-Methylpentane	AlBr ₃	(5.9–8.7%)		room
3-Methylpentane	(96%) H ₂ SO ₄ + (4%) H ₂ O		500	
2,2-Dimethylbutane	AlBr ₃	(5.9–8.7%)		room
2,2-Dimethylbutane	AlCl ₃ HCl		0–16	80
2,2-Dimethylbutane	97% H ₂ SO ₄ + 3% H ₂ O		2.5	50 (?)
2,3-Dimethylbutane	AlBr ₃	(5.9–8.7%)		room
2,3-Dimethylbutane	AlCl ₃ HCl		16	80
<i>n</i> -Heptane	AlCl ₃ H ₂ O	(26.5%) (1.0%)	24	100
<i>n</i> -Heptane	AlCl ₃ Ethyl chloride (experiment No. 1) Propyl chloride (experiment No. 2) Isopropyl chloride (experiment No. 3) Butyl chloride (experiment No. 4)			room
<i>n</i> -Heptane	AlCl ₃ HCl	(9.2%) (?)	5	40
<i>n</i> -Heptane	AlCl ₃	(9.09%)	2 (?)	40
<i>n</i> -Heptane	AlCl ₃	(9.09%)	2 (?)	80
<i>n</i> -Heptane	AlCl ₃	(4.76%)	2 (?)	100
<i>n</i> -Heptane	AlCl ₃	(9.09%)	2 (?)	100
<i>n</i> -Heptane	AlCl ₃	(13.0%)	2 (?)	100
<i>n</i> -Heptane	AlCl ₃	(9.09%)	2 (?)	120
<i>n</i> -Heptane	AlCl ₃	(9.09%)	2 (?)	140
<i>n</i> -Heptane	AlCl ₃	(38.7%)		96
<i>n</i> -Heptane	AlCl ₃	(1%)	3	220
<i>n</i> -Heptane	AlCl ₃			100

Continuedtion of Alkanes—Continuedtion of Alkanes—Continuedtion of Alkanes—Con

Products	Products	Products	Products
Percent by weight on original alkane	Percent by weight on original alkane	Percent by weight on original alkane	Percent by weight on original alkane
Isomer Products	Isomer Products	Isomer Products	Isomer Products
2-Methylpentane (306)	2-Methylpentane (306)	2-Methylpentane (306)	2-Methylpentane (306)
2-Methylpentane (306)	2-Methylpentane (306)	2-Methylpentane (306)	2-Methylpentane (306)
3-Methylpentane (366)	3-Methylpentane (366)	3-Methylpentane (366)	3-Methylpentane (366)
2-Methylpentane (366)	2-Methylpentane (366)	2-Methylpentane (366)	2-Methylpentane (366)
2,3-Dimethylbutane (520a)	2,3-Dimethylbutane (520a)	2,3-Dimethylbutane (520a)	2,3-Dimethylbutane (520a)
No isomers (11)	No isomers (11)	No isomers (11)	No isomers (11)
(liquid phase)	(liquid phase)	(liquid phase)	(liquid phase)
Isomers (109%) (5024)	Isomers (109%) (5024)	Isomers (109%) (5024)	Isomers (109%) (5024)
Higher-boiling hydrocarbons (7%)	Higher-boiling hydrocarbons (7%)	Higher-boiling hydrocarbons (7%)	Higher-boiling hydrocarbons (7%)
2-Methylpentane (306)	2-Methylpentane (306)	2-Methylpentane (306)	2-Methylpentane (306)
2,3-Dimethylbutane (520a)	2,3-Dimethylbutane (520a)	2,3-Dimethylbutane (520a)	2,3-Dimethylbutane (520a)
2,3-Dimethylbutane (520a)	2,3-Dimethylbutane (520a)	2,3-Dimethylbutane (520a)	2,3-Dimethylbutane (520a)
2-Methylpentane (306)	2-Methylpentane (306)	2-Methylpentane (306)	2-Methylpentane (306)
2-Methylpentane (306)	2-Methylpentane (306)	2-Methylpentane (306)	2-Methylpentane (306)
Hydrogen chloride (0.08%)	Hydrogen chloride (0.08%)	Hydrogen chloride (0.08%)	Hydrogen chloride (0.08%)
Propane	Propane	Propane	Propane
Isobutane	Isobutane	Isobutane	Isobutane
Pentane and hexane fractions	Pentane and hexane fractions	Pentane and hexane fractions	Pentane and hexane fractions
High-boiling cyclanes	High-boiling cyclanes	High-boiling cyclanes	High-boiling cyclanes
Unsaturated hydrocarbons	Unsaturated hydrocarbons	Unsaturated hydrocarbons	Unsaturated hydrocarbons
Methylhexane (401)	Methylhexane (401)	Methylhexane (401)	Methylhexane (401)
Methylpentane (1.7%)	Methylpentane (1.7%)	Methylpentane (1.7%)	Methylpentane (1.7%)
From combined experiments	From combined experiments	From combined experiments	From combined experiments

Isomers (3.0%) (546a)	Isomers (3.0%) (546a)	Isomers (3.0%) (546a)	Isomers (3.0%) (546a)
n-Hexane	n-Hexane	n-Hexane	n-Hexane
Isopentane	Isopentane	Isopentane	Isopentane
Isohexanes	Isohexanes	Isohexanes	Isohexanes
63.4% Heptane	63.4% Heptane	63.4% Heptane	63.4% Heptane
Higher n-alkanes	Higher n-alkanes	Higher n-alkanes	Higher n-alkanes
Higher isoalkanes	Higher isoalkanes	Higher isoalkanes	Higher isoalkanes
Isomers (109%) (39a)	Isomers (109%) (39a)	Isomers (109%) (39a)	Isomers (109%) (39a)
91.7% Heptane	91.7% Heptane	91.7% Heptane	91.7% Heptane
Isomers (10.4%) over (39a)	Isomers (10.4%) over (39a)	Isomers (10.4%) over (39a)	Isomers (10.4%) over (39a)
63.2% Heptane	63.2% Heptane	63.2% Heptane	63.2% Heptane
Isomers (2.1%) over (39a)	Isomers (2.1%) over (39a)	Isomers (2.1%) over (39a)	Isomers (2.1%) over (39a)
37.1% Heptane	37.1% Heptane	37.1% Heptane	37.1% Heptane
Isomers (2.3%) over (39a)	Isomers (2.3%) over (39a)	Isomers (2.3%) over (39a)	Isomers (2.3%) over (39a)
35.8% Heptane	35.8% Heptane	35.8% Heptane	35.8% Heptane
Isomers (2.2%) over (39a)	Isomers (2.2%) over (39a)	Isomers (2.2%) over (39a)	Isomers (2.2%) over (39a)
30.5% Heptane	30.5% Heptane	30.5% Heptane	30.5% Heptane
Isomers (2.9%) over (39a)	Isomers (2.9%) over (39a)	Isomers (2.9%) over (39a)	Isomers (2.9%) over (39a)

Table 6. Isomeriza

Reactants		Catalyst (Per cent by weight on alkane + catalyst)	Contact Time (hours)	Temp. (°C.)
Alkane				
<i>n</i> -Heptane	ZnCl ₂	(5%)	6	300
<i>n</i> -Heptane	ZnCl ₂	(5%)	7	400
<i>n</i> -Heptane	MoS ₃	(5%)	7	400
<i>n</i> -Heptane	CuO	(5%)	2	400
	MoS ₂	(9.0%)		
<i>n</i> -Heptane (not pure)	MoS ₃	(5%)	3	420
<i>n</i> -Heptane (not pure)	MoS ₃	(5%)	7	420
<i>n</i> -Heptane (not pure)	MoS ₃	(5%)	14	420
2,4-Dimethylpentane	97% H ₂ SO ₄ + 3% H ₂ O		2	50
<i>n</i> -Octane	Activated-carbon		5-6 drops feed per min. (3 passes)	300-310
<i>n</i> -Octane	20% Pt + 80% activated-carbon		5-6 drops feed per min. (3 passes)	300-310
<i>n</i> -Octane	Unlined steel apparatus No. 1		2	450
<i>n</i> -Octane	Ag-lined steel apparatus No. 1		2	325
<i>n</i> -Octane	Ag-lined steel apparatus No. 1		2	450
<i>n</i> -Octane	Ag-lined steel apparatus No. 1		2	450
<i>n</i> -Octane	Ag-lined steel apparatus No. 1		3.7	450
<i>n</i> -Octane	Steel autoclave		2.15	475
<i>n</i> -Octane	Cu tube		2.6 min.	591
<i>n</i> -Octane	23% Ni + 77% Al ₂ O ₃		5-6 drops feed per min. (3 passes)	300-310
<i>n</i> -Octane	21% Ni + 79% ZnO		5-6 drops feed per min. (3 passes)	300-310
<i>n</i> -Octane	Al ₂ O ₃		5-6 drops feed per min. (3 passes)	300-310
<i>n</i> -Octane	Al ₂ O ₃		6 cc. feed per hour	300-310
<i>n</i> -Octane	MoS ₃	(5%)	3	410
<i>n</i> -Octane	MoS ₃	(5%)	3	440
<i>n</i> -Octane	Durax-glass bomb tube		24	280
<i>n</i> -Octane	Porcelain tube used		1/12 drop feed per sec.	450

Continuation of Alkanes—Continued

Continuation of Alkanes—Continued

Continuation of Alkanes—Continued

Continuation of Alkanes—Continued

Products	Products	Products	Products
on original pressure	on original pressure	on original pressure	on original pressure
Other Products	Other Products	Other Products	Other Products
(437) and higher-boiling	(437) and higher-boiling	(437) and higher-boiling	(437) and higher-boiling
below 50 u.s.gal. (187.5 l.)	below 50 u.s.gal. (187.5 l.)	below 50 u.s.gal. (187.5 l.)	below 50 u.s.gal. (187.5 l.)
(437) and higher-boiling	(437) and higher-boiling	(437) and higher-boiling	(437) and higher-boiling
below 50 u.s.gal. (187.5 l.)	below 50 u.s.gal. (187.5 l.)	below 50 u.s.gal. (187.5 l.)	below 50 u.s.gal. (187.5 l.)
(437) and higher-boiling	(437) and higher-boiling	(437) and higher-boiling	(437) and higher-boiling
below 50 u.s.gal. (187.5 l.)	below 50 u.s.gal. (187.5 l.)	below 50 u.s.gal. (187.5 l.)	below 50 u.s.gal. (187.5 l.)
(N ₂) (407) (11.9%)	(N ₂) (407) (11.9%)	(N ₂) (407) (11.9%)	(N ₂) (407) (11.9%)
140 (11.9%)	140 (11.9%)	140 (11.9%)	140 (11.9%)
(H ₂) (437) (11.9%)	(H ₂) (437) (11.9%)	(H ₂) (437) (11.9%)	(H ₂) (437) (11.9%)
n- Recovered (85.0%)	n- Recovered (85.0%)	n- Recovered (85.0%)	n- Recovered (85.0%)
Higher-boiling products	Higher-boiling products	Higher-boiling products	Higher-boiling products
(437) (11.9%)	(437) (11.9%)	(437) (11.9%)	(437) (11.9%)
n- Recovered (74.0%)	n- Recovered (74.0%)	n- Recovered (74.0%)	n- Recovered (74.0%)
Higher-boiling products	Higher-boiling products	Higher-boiling products	Higher-boiling products
(437) (11.9%)	(437) (11.9%)	(437) (11.9%)	(437) (11.9%)
n- Recovered (69.0%)	n- Recovered (69.0%)	n- Recovered (69.0%)	n- Recovered (69.0%)
Higher-boiling products	Higher-boiling products	Higher-boiling products	Higher-boiling products
(437) (11.9%)	(437) (11.9%)	(437) (11.9%)	(437) (11.9%)
methylpentane (95c) (659) (15.9%)	methylpentane (95c) (659) (15.9%)	methylpentane (95c) (659) (15.9%)	methylpentane (95c) (659) (15.9%)
1 (15.9%)	1 (15.9%)	1 (15.9%)	1 (15.9%)
(H ₂) (659) (15.9%)	(H ₂) (659) (15.9%)	(H ₂) (659) (15.9%)	(H ₂) (659) (15.9%)
1 (15.9%)	1 (15.9%)	1 (15.9%)	1 (15.9%)
(H ₂) (380) (11.9%)	(H ₂) (380) (11.9%)	(H ₂) (380) (11.9%)	(H ₂) (380) (11.9%)
Gases 123 (380) (11.9%)	Gases 123 (380) (11.9%)	Gases 123 (380) (11.9%)	Gases 123 (380) (11.9%)
Liquids 8 (380) (11.9%)	Liquids 8 (380) (11.9%)	Liquids 8 (380) (11.9%)	Liquids 8 (380) (11.9%)
Gases 74 (380) (11.9%)	Gases 74 (380) (11.9%)	Gases 74 (380) (11.9%)	Gases 74 (380) (11.9%)
Liquids 7 (380) (11.9%)	Liquids 7 (380) (11.9%)	Liquids 7 (380) (11.9%)	Liquids 7 (380) (11.9%)
Gases 69 (380) (11.9%)	Gases 69 (380) (11.9%)	Gases 69 (380) (11.9%)	Gases 69 (380) (11.9%)
Liquids 6 (380) (11.9%)	Liquids 6 (380) (11.9%)	Liquids 6 (380) (11.9%)	Liquids 6 (380) (11.9%)
Gases 99 (380) (11.9%)	Gases 99 (380) (11.9%)	Gases 99 (380) (11.9%)	Gases 99 (380) (11.9%)
Liquids 9 (380) (11.9%)	Liquids 9 (380) (11.9%)	Liquids 9 (380) (11.9%)	Liquids 9 (380) (11.9%)
Gases 201 (380) (11.9%)	Gases 201 (380) (11.9%)	Gases 201 (380) (11.9%)	Gases 201 (380) (11.9%)
Liquids 20 (380) (11.9%)	Liquids 20 (380) (11.9%)	Liquids 20 (380) (11.9%)	Liquids 20 (380) (11.9%)
Gases 70 (380) (11.9%)	Gases 70 (380) (11.9%)	Gases 70 (380) (11.9%)	Gases 70 (380) (11.9%)
Liquids 7 (380) (11.9%)	Liquids 7 (380) (11.9%)	Liquids 7 (380) (11.9%)	Liquids 7 (380) (11.9%)
Gases 1 (380) (11.9%)	Gases 1 (380) (11.9%)	Gases 1 (380) (11.9%)	Gases 1 (380) (11.9%)
Liquids 1 (380) (11.9%)	Liquids 1 (380) (11.9%)	Liquids 1 (380) (11.9%)	Liquids 1 (380) (11.9%)
1 (659) (15.9%)	1 (659) (15.9%)	1 (659) (15.9%)	1 (659) (15.9%)
(H ₂) (659) (15.9%)	(H ₂) (659) (15.9%)	(H ₂) (659) (15.9%)	(H ₂) (659) (15.9%)
below 1.0% (659) (15.9%)	below 1.0% (659) (15.9%)	below 1.0% (659) (15.9%)	below 1.0% (659) (15.9%)
(H ₂) (659) (15.9%)	(H ₂) (659) (15.9%)	(H ₂) (659) (15.9%)	(H ₂) (659) (15.9%)
Combined (659) (15.9%)	Combined (659) (15.9%)	Combined (659) (15.9%)	Combined (659) (15.9%)
about 5.0% (659) (15.9%)	about 5.0% (659) (15.9%)	about 5.0% (659) (15.9%)	about 5.0% (659) (15.9%)

Table 6. Isomeriza

Alkane	Reactants		Contact Time (hours)	Temp. (°C.)
	Catalyst (Per cent by weight on alkane + catalyst)			
<i>n</i> -Octane	Porcelain tube used		1/12 drop feed per sec.	500
<i>n</i> -Octane	Porcelain tube used		1/13 drop feed per sec.	550
<i>n</i> -Octane	AlBr ₃ + HBr	(20%)	120	room
<i>n</i> -Octane	AlCl ₃	(10%)	1.5	20
<i>n</i> -Octane	HCl	(8%)	1	20
<i>n</i> -Octane	AlCl ₃	(4%)	4	20
<i>n</i> -Octane	Propyl chloride	(10%)	4	20
<i>n</i> -Octane	AlCl ₃	(10%)	22	20
<i>n</i> -Octane	HCl	(10%)	22	20
<i>n</i> -Octane	AlCl ₃	(10%)	6	20
<i>n</i> -Octane	PbSO ₄ . 2HCl	(10%)	8	20
<i>n</i> -Octane	HCl	(10%)	22	20
<i>n</i> -Octane	AlCl ₃	(5%)	22	20
<i>n</i> -Octane	HCl	(10%)	22	20
<i>n</i> -Octane	AlCl ₃	(10%)	22	20
<i>n</i> -Octane	PbSO ₄ . 2HCl	(10%)	24	20
<i>n</i> -Octane	AlCl ₃	(10%)	96	20
<i>n</i> -Octane	HCl	(10%)	140	room
<i>n</i> -Octane	AlCl ₃ + HCl	(20%)	6	50-55
<i>n</i> -Octane	AlCl ₃	(9.09%)		
<i>n</i> -Octane	HCl	(?%)		
<i>n</i> -Octane	AlCl ₃	(9.09%)	2 (?)	40
<i>n</i> -Octane	AlCl ₃	(9.09%)	2	80
<i>n</i> -Octane	AlCl ₃	(4.76%)	2 (?)	100
<i>n</i> -Octane	AlCl ₃	(9.09%)	2 (?)	100
<i>n</i> -Octane	AlCl ₃	(13.0%)	2 (?)	100
<i>n</i> -Octane	AlCl ₃	(9.09%)	2 (?)	120
<i>n</i> -Octane	AlCl ₃	(9.09%)	2 (?)	140
<i>n</i> -Octane	AlCl ₃	(5%)	3	405-410
<i>n</i> -Octane	ZnCl ₂	(5%)	3	410

of Alkanes—Continued of Alkanes—Continued of Alkanes—Continued

[illegible]

Table 6. Isomeriza

Feed Type	Reactor	Temp.	Contact Time	Feed Type	Reactor	Temp.	Contact Time	Feed Type	Reactor	Temp.	Contact Time
alkane + catalyst	(0.00%)	(0.00%)	(0.00%)	alkane + catalyst	(0.00%)	(0.00%)	(0.00%)	alkane + catalyst	(0.00%)	(0.00%)	(0.00%)
2 (?)	2-Methylheptane	(0.00%)	(0.00%)	2 (?)	2-Methylheptane	(0.00%)	(0.00%)	2 (?)	2-Methylheptane	(0.00%)	(0.00%)
2 (?)	2-Methylheptane	(0.00%)	(0.00%)	2 (?)	2-Methylheptane	(0.00%)	(0.00%)	2 (?)	2-Methylheptane	(0.00%)	(0.00%)
2 (?)	2-Methylheptane	(4.10%)	(4.10%)	2 (?)	2-Methylheptane	(4.10%)	(4.10%)	2 (?)	2-Methylheptane	(4.10%)	(4.10%)
2 (?)	2-Methylheptane	(9.10%)	(9.10%)	2 (?)	2-Methylheptane	(9.10%)	(9.10%)	2 (?)	2-Methylheptane	(9.10%)	(9.10%)
2 (?)	2-Methylheptane	(13.10%)	(13.10%)	2 (?)	2-Methylheptane	(13.10%)	(13.10%)	2 (?)	2-Methylheptane	(13.10%)	(13.10%)
2 (?)	2-Methylheptane	(9.130%)	(9.130%)	2 (?)	2-Methylheptane	(9.130%)	(9.130%)	2 (?)	2-Methylheptane	(9.130%)	(9.130%)
2 (?)	2-Methylheptane	(9.140%)	(9.140%)	2 (?)	2-Methylheptane	(9.140%)	(9.140%)	2 (?)	2-Methylheptane	(9.140%)	(9.140%)
2 (?)	2,2,4-Trimethylpentane	(9.040%)	(9.040%)	2 (?)	2,2,4-Trimethylpentane	(9.040%)	(9.040%)	2 (?)	2,2,4-Trimethylpentane	(9.040%)	(9.040%)
2 (?)	2,2,4-Trimethylpentane	(9.050%)	(9.050%)	2 (?)	2,2,4-Trimethylpentane	(9.050%)	(9.050%)	2 (?)	2,2,4-Trimethylpentane	(9.050%)	(9.050%)
2 (?)	2,2,4-Trimethylpentane	(4.100%)	(4.100%)	2 (?)	2,2,4-Trimethylpentane	(4.100%)	(4.100%)	2 (?)	2,2,4-Trimethylpentane	(4.100%)	(4.100%)
2 (?)	2,2,4-Trimethylpentane	(9.100%)	(9.100%)	2 (?)	2,2,4-Trimethylpentane	(9.100%)	(9.100%)	2 (?)	2,2,4-Trimethylpentane	(9.100%)	(9.100%)
2 (?)	2,2,4-Trimethylpentane	(13.100%)	(13.100%)	2 (?)	2,2,4-Trimethylpentane	(13.100%)	(13.100%)	2 (?)	2,2,4-Trimethylpentane	(13.100%)	(13.100%)
2 (?)	2,2,4-Trimethylpentane	(9.130%)	(9.130%)	2 (?)	2,2,4-Trimethylpentane	(9.130%)	(9.130%)	2 (?)	2,2,4-Trimethylpentane	(9.130%)	(9.130%)
2 (?)	2,2,4-Trimethylpentane	(9.140%)	(9.140%)	2 (?)	2,2,4-Trimethylpentane	(9.140%)	(9.140%)	2 (?)	2,2,4-Trimethylpentane	(9.140%)	(9.140%)

Table 6. Isomeriza

Type	Reaction	Temp
alkane + catalyst	(95%)	
2 (?)	(9.04%)	
2-Methylheptane		
2 (?)	(9.03%)	
2-Methylheptane		
2 (?)	(4.19%)	
2-Methylheptane		
2 (?)	(9.10%)	
2-Methylheptane		
2 (?)	(13.97%)	
2-Methylheptane		
2 (?)	(9.12%)	
2-Methylheptane		
2 (?)	(9.14%)	
2-Methylheptane		
2 (?)	(9.04%)	
2,2,4-Trimethylp		
2 (?)	(9.03%)	
2,2,4-Trimethylp		
2 (?)	(4.19%)	
2,2,4-Trimethylp		
2 (?)	(9.10%)	
2,2,4-Trimethylp		
2 (?)	(4.19%)	
2,2,4-Trimethylp		
2 (?)	(9.12%)	
2,2,4-Trimethylp		
2 (?)	(9.14%)	
2,2,4-Trimethylp		
feed	350	
hour-12	Ni + Al ₂	
Decane		

Table 6. Isomeriza

[illegible]

tion of Alkanes—Continued

Pressure (atms.)		Products		Refer- ences
		(Per cent by weight on original alkane)	Other Products	
	Isomers			
1	No isomers		Gas (trace)	(39a)
			2-Methylheptane (96%)	
over 1	Isomers	(2.9%)	Gas (3%)	(39a)
			2-Methylheptane (55%)	
over 1	Isomers	(4.1%)	Gas (3.4%)	(39a)
			2-Methylheptane (38%)	
over 1	Isomers	(4.0%)	Gas (3.5%)	(39a)
			2-Methylheptane (36%)	
over 1	Isomers	(6.0%)	Gas (3.7%)	(39a)
			2-Methylheptane (34%)	
over 1	Isomers	(13%)	Gas (4.7%)	(39a)
			2-Methylheptane (25%)	
over 1	Isomers	(16%)	Gas (4.9%)	(39a)
			2-Methylheptane (19%)	
over 1	Isomers	(4.5%)	Gas (1.5%)	(39a)
			2,2,4-Trimethylpentane (85%)	
over 1	Isomers	(6.5%)	Gas (2.7%)	(39a)
			2,2,4-Trimethylpentane (58.7%)	
over 1	Isomers	(10.5%)	Gas (4.0%)	(39a)
			2,2,4-Trimethylpentane (42.0%)	
over 1	Isomers	(12.9%)	Gas (4.0%)	(39a)
			2,2,4-Trimethylpentane (38.6%)	
over 1	Isomers	(12.7%)	Gas (3.9%)	(39a)
			2,2,4-Trimethylpentane (38.1%)	
over 1	Isomers	(13.6%)	Gas (4.6%)	(39a)
			2,2,4-Trimethylpentane (31.8%)	
over 1	Isomers	(15.0%)	Gas (4.8%)	(39a)
			2,2,4-Trimethylpentane (27.8%)	
1	Isomers	(1.6%)	Hydrogen	(319)
(N ₂)			Methane	
			<i>n</i> -Decane (44%)	
			Aromatics (6.0%)	

Table 10. Isomeriza

Alkene	Reactants		Contact Time (hours)	Temp. (°C.)
		Catalyst (Per cent by weight on alkene + catalyst)		
Propene				400-405
Propene				410
Propene			59-105 min.	600
Butene-1		Quartz tube		550
Butene-1		Quartz tube	100 vols. feed per vol. re- action-space per hour	550
Butene-1			100 vols. feed per vol. re- action-space per hour	400-600 (prefer- ably 575)
Butene-1				650
Butene-1				700
Butene-1		Ni	19 min.	133
Butene-1		H ₂ (quantity equal to butene-1)		
Butene-1		CaO	100 vols. feed per vol. re- action-space per hour	400-500
Butene-1		CaO		420
Butene-1		Porcelain tube used		
Butene-1		CaO	100 vols. feed per vol. re- action-space per hour	420
Butene-1		Porcelain tube used		
Butene-1		Bauxite		400
		SiO ₂		
		TiO ₂		
		Difficultly-reducible metal oxides		
		Borates		
		Phosphates		
		Silicates		
		(used individually)		
Butene-1		Difficultly-reducible metal oxides	100 vols. feed per vol. re- action-space per hour	400-500
		Neutral borates		
		Neutral phosphates		
		Neutral silicates		
		(used individually)		
Butene-1		Aluminum phosphate on pumice		400
Butene-1		Aluminum phosphate on pumice (Bauxite may also be employed)	100 vols. feed per vol. re- action-space per hour	400
Butene-1		Aluminum phosphate		427
Butene-1		Aluminum sulfate		270-290
Butene-1		75% ZnCl ₂ + 25% H ₂ O		100
Butene-1		75% C ₆ H ₅ SO ₃ H + 25% H ₂ O		76
Butene-1		71% HClO ₄ + 29% H ₂ O		21
Butene-1		H ₃ PO ₄		78
Butene-1		H ₃ PO ₄		135
Butene-1		H ₃ PO ₄		249
Butene-1		H ₃ PO ₄ on diatomaceous earth	206 sec.	347 or
cis-Butene-2	(47.2%)	"Pyrex" reaction-vessel	500 min.	390
trans-Butene-2	(52.8%)			650
cis-Butene-2	(38.0%)			

tion of Alkenes

Pressure (atms.)	Products (Per cent by weight on original alkene)			Refer- ences
	Isomers	Other Products		
	Cyclopropane			(166)
	Cyclopropane	(about 60%)		(203)
1	No isomer		Propene Polymers	(590)
	Butene-2	(87%)	Butene-1 Polymer	(11%) (266)
1	Butene-2	(87%)	Butene-1 Polymer	(2%) (267)
1	Butene-2			(267)
	<i>cis</i> -Butene-2	(4.4%)	Butene-1	(43.4%) (264)
	<i>trans</i> -Butene-2	(7.1%)		
	Butene-2	(2.4%)	Butene-1	(12.7%) (264)
	Butene-2		<i>n</i> -Butane	(10%) (600)
1	Butene-2			(267)
	Butene-2	(92%)	Polymer	(266)
1	Butene-2	(92%)	Polymer	(267)
	Butene-2			(266)
1	Butene-2			(267)
1	Butene-2	(almost 100%)		(266)
	Butene-2	(almost 100%)		(267)
1	Butene-2	(70-80%)	Butene-1	(20-30%) (285)
1	Butene-2			(212)
1	Butene-2	(5%)		(285)
1	Butene-2	(13%)		(285)
1	Butene-2	(21%)		(285)
1	Butene-2	(12%)	Butene-1	(88%) (285)
1	Butene-2	(60%)	Butene-1	(40%) (285)
7.8	Butene-2	(100%)		(285)
sub-atm.	<i>cis</i> -Butene-2	(47.2%)		(307)
	<i>trans</i> -Butene-2	(52.8%)		
	Butene-1	(10.7%)	<i>cis</i> -Butene-2	(22.0%) (264)

Table 10. Isomeriza

Reactants		Catalyst (Per cent by weight on alkene + catalyst)	Contact Time (hours)	Temp. (°C.)
Alkene				
<i>trans</i> -Butene-2	(62.0%)	H ₃ PO ₄		700
<i>cis</i> -Butene-2	(38.0%)			
<i>trans</i> -Butene-2	(62.0%)			100
<i>cis</i> -Butene-2				
<i>n</i> -Butenes (various mixtures with more than or less than 96 per cent of Butene-2)		Ni wire of 0.1 mm. diameter H ₂		76
Butene-1	(15.2%)	Activated SiO ₂ -Al ₂ O ₃	525 cc. feed per cc. catalyst per hour	385
Butene-2	(83.8%)			
Butene-1	(15.2%)	Activated SiO ₂ -Al ₂ O ₃	200 cc. feed per cc. catalyst per hour	400
Butene-2	(83.8%)			
Butene-1	(15.2%)	Activated SiO ₂ -Al ₂ O ₃	230 cc. feed per cc. catalyst per hour	450
Butene-2	(83.8%)			
Butene-1	(15.2%)	Activated SiO ₂ -Al ₂ O ₃	230 cc. feed per cc. catalyst per hour	500
Butene-2	(83.8%)			
Butene-1	(15.2%)	Activated SiO ₂ -Al ₂ O ₃	225 cc. feed per cc. catalyst per hour	550
Butene-2	(83.8%)			
Butene-1	(15.2%)	Activated SiO ₂ -Al ₂ O ₃	205 cc. feed per cc. catalyst per hour	600
Butene-2	(83.8%)			
Butene-1	(15.2%)	Activated SiO ₂ -Al ₂ O ₃	1160 cc. feed per cc. cata- lyst per hour	600
Butene-2	(83.8%)			

tion of Alkenes—Continued

Pressure (atms.)	Products				Refer- ences
	Isomers	(Per cent by weight on original alkene)		Other Products	
				<i>trans</i> -Butene-2 (34.0%)	
	Butene-1	(8.7%)		<i>cis</i> -Butene-2 (7.6%)	(264)
				<i>trans</i> -Butene-2 (11.8%)	
1	Butene-1	(6.6%)		<i>cis</i> -Butene-2 (87.4%)	(285)
	<i>trans</i> -Butene-2	(6.0%)			
	Butene-2				
	Butene-1			<i>n</i> -Butane	(600a)
	"Equilibrium conditions"				
1	Isobutene	(8.0%)		C ₃ H ₆ (2.3%)	(158)
				C ₃ H ₈ (0.5%)	
				C ₄ H ₆ + <i>n</i> -butenes (74.2%)	
				C ₄ H ₁₀ fraction (0.9%)	
				High-boiling fraction (14.0%)	
1	Isobutene	(11.6%)		H ₂ (0.1%)	(158)
				CH ₄ (0.1%)	
				C ₃ H ₆ (6.4%)	
				C ₃ H ₈ (0.7%)	
				C ₄ H ₆ (0.5%)	
				<i>n</i> -Butenes (57.2%)	
				C ₄ H ₁₀ (3.2%)	
				High-boiling fraction (20.2%)	
1	Isobutene	(14.1%)		C ₃ H ₆ (10.7%)	(158)
				C ₃ H ₈ (2.4%)	
				C ₄ H ₆ (0.2%)	
				<i>n</i> -Butenes (42.3%)	
				C ₄ H ₁₀ (6.0%)	
				High-boiling fraction (24.3%)	
1	Isobutene	(15.9%)		C ₂ H ₄ (0.04%)	(158)
				C ₂ H ₆ (0.5%)	
				C ₃ H ₆ (14.4%)	
				C ₃ H ₈ (2.2%)	
				C ₄ H ₆ (0.3%)	
				<i>n</i> -Butenes (39.6%)	
				C ₄ H ₁₀ (6.5%)	
				High-boiling fraction (20.5%)	
1	Isobutene	(15.0%)		H ₂ (0.2%)	(158)
				CH ₄ (2.6%)	
				C ₂ H ₄ (1.1%)	
				C ₂ H ₆ (1.2%)	
				C ₃ H ₆ (14.6%)	
				C ₃ H ₈ (1.4%)	
				C ₄ H ₆ (0.3%)	
				<i>n</i> -Butenes (40.4%)	
				C ₄ H ₁₀ (8.8%)	
				High-boiling fraction (14.4%)	
1	Isobutene	(14.2%)		H ₂ (0.9%)	(158)
				CH ₄ (7.8%)	
				C ₂ H ₄ (2.0%)	
				C ₂ H ₆ (2.7%)	
				C ₃ H ₆ (15.3%)	
				C ₃ H ₈ (2.9%)	
				C ₄ H ₆ + <i>n</i> -butenes (36.8%)	
				C ₄ H ₁₀ (8.5%)	
				High-boiling fraction (8.9%)	
1	Isobutene	(17.1%)		H ₂ (0.04%)	(158)
				CH ₄ (0.8%)	
				C ₂ H ₄ (0.2%)	
				C ₂ H ₆ (0.8%)	
				C ₃ H ₆ (12.4%)	
				C ₃ H ₈ (1.4%)	

Table 10. Isomeriza

Reactants		Catalyst (Per cent by weight on alkene + catalyst)	Contact Time (hours)	Temp. (°C.)
Alkene				
Butene-1 and -2 (<i>Continued</i>)				
<i>n</i> -Butenes		Al ₂ O ₃ Steam	116 sec.	294
<i>n</i> -Butenes		Aluminum sulfate Steam	137 sec.	294
<i>n</i> -Butenes		Glukhov clay Steam	138 sec.	294
<i>n</i> -Butenes		"Floridin" Steam	134 sec.	294
<i>n</i> -Butenes Isobutene <i>n</i> -Butane	(50.9%) (16.1%) (33%)	Permutite	58 sec.	400
<i>n</i> -Butenes Isobutene <i>n</i> -Butane	(31.2%) (28.8%) (40%)	Permutite	59 sec.	400
<i>n</i> -Butenes Isobutene <i>n</i> -Butane	(31.2%) (28.8%) (40%)	Permutite	170 sec.	400
<i>n</i> -Butenes <i>n</i> -Butane	(50%) (50%)	Sodium permutite	183 sec.	450
<i>n</i> -Butenes <i>n</i> -Butane	(50%) (50%)	Sodium permutite	183 sec.	450
<i>n</i> -Butenes		76.2% H ₃ PO ₄ + 23.8% charcoal (applied at 300°) Steam	130 sec.	294
<i>n</i> -Butenes		33.3% H ₃ PO ₄ + 67.7% charcoal (applied at 450°) Steam	122 sec.	294
<i>n</i> -Butenes		H ₃ PO ₄ + silicate (dried 18–20 hours at 280–300°) Steam	120 sec.	294
<i>n</i> -Butenes		H ₃ PO ₄ + silicate (dried 2–3 hours at 280–300°) Steam	144 sec.	294
<i>n</i> -Butenes		H ₃ PO ₄ + silicate (dried 2–3 hours at 280–300°) Steam	280 sec.	294
<i>n</i> -Butenes		H ₃ PO ₄ + silicate (dried 2–3 hours at 280–300°) Steam	288 sec.	294
<i>n</i> -Butenes		H ₃ PO ₄ on kieselguhr Steam (equimolar with butenes)	10 sec.	325
<i>n</i> -Butenes		H ₃ PO ₄ on kieselguhr Steam (equimolar with butenes)	40 vols. feed per vol. cata- lyst per hour	325
Butene-1 and/or Butene-2		H ₃ PO ₃ , HPO ₃ , H ₃ PO ₄ , or H ₄ P ₂ O ₇ on carbon, silica gel, diatomace- ous earth, or kieselguhr;		250–550 (325 optimum)

tion of Alkenes—Continued

Pressure (atms.)	Products		References
	Isomers	(Per cent by weight on original alkene) Other Products	
		C ₄ H ₆ (0.8%)	
		<i>n</i> -Butenes (50.7%)	
		C ₄ H ₁₀ (3.0%)	
		High-boiling fraction (12.7%)	
1	Isobutene <i>n</i> -Butenes = 0.00847	Other gases (199)	
		Polymers (200)	
1	Isobutene <i>n</i> -Butenes = 0.120	C ₂ H ₄ (199)	
		Other gases (200)	
		Polymers (15%)	
1	Isobutene <i>n</i> -Butenes = 0.0810	C ₂ H ₄ (199)	
		Other gases (200)	
		Polymers (37%)	
1	Isobutene <i>n</i> -Butenes = 0.0655	C ₂ H ₄ (199)	
		Other gases (200)	
		Polymers (34%)	
	Isobutene (17.1%)	<i>n</i> -Butenes (48.9%)	(529a)
	Isobutene <i>n</i> -Butenes = 0.351	<i>n</i> -Butane (33%?)	
		Polymers (1%?)	
	<i>n</i> -Butenes (31.4%)	Isobutene (25.6%)	(529a)
	Isobutene <i>n</i> -Butenes = 0.818	<i>n</i> -Butane (40%?)	
		Polymers (3%?)	
	Isobutene <i>n</i> -Butenes = 0.725	<i>n</i> -Butenes (29.6%)	(529a)
		Isobutene (21.4%)	
		<i>n</i> -Butane (40%?)	
		Polymers (9%?)	
1	Isobutene (33% by vol. of exit-gas alkenes)		(257a)
	Isobutene		(421a)
			(417a)
1	Isobutene <i>n</i> -Butenes = 0.212	C ₂ H ₄ (199)	
		Other gases (200)	
		Polymers (2%)	
1	Isobutene <i>n</i> -Butenes = 0.531	Other gases (large %)	(199)
		Polymers (43%)	(200)
1	Isobutene <i>n</i> -Butenes = 0.173	C ₂ H ₄ (199)	
		Other gases (200)	
		Polymers (2%)	
1	Isobutene <i>n</i> -Butenes = 0.895	C ₂ H ₄ (199)	
		Other gases (200)	
		Polymers (36%)	
1	Isobutene <i>n</i> -Butenes = 0.652	C ₂ H ₄ (199)	
		Other gases (200)	
		Polymers (21%)	
1	Isobutene <i>n</i> -Butenes = 0.420	C ₂ H ₄ (199)	
		Other gases (200)	
		Polymers (7%)	
1	Isobutene (33%)	<i>n</i> -Butenes (67%)	(417)
		Liquid (trace)	
1	Isobutene (33% by vol. of exit-gas)	<i>n</i> -Butenes (67% by vol. of exit-gas)	(420)
		Liquid (trace)	
1-10	Isobutene	Isooctenes	(417)

Table 10. Isomeriza

Reactants		Catalyst (Per cent by weight on alkene + catalyst)	Contact Time (hours)	Temp. (°C.)
Alkene				
Butene-1 and/or -2 (<i>Continued</i>)		Added phosphotungstic or phosphomolybdic acids if desired; Steam		
<i>n</i> -Butenes		H ₃ PO ₄ on kieselguhr	50 sec.	325
<i>n</i> -Butenes	(51.4%)	82% H ₃ PO ₄ (conc. about 89%)	80.0 sec.	275
<i>n</i> -Butane	(48.6%)	+18% kieselguhr (dried at 250°) (heated at 275° in vacuo before use)		
<i>n</i> -Butenes	(51.4%)	82% H ₃ PO ₄ (conc. about 89%)	10.0 sec.	275
<i>n</i> -Butane	(48.6%)	+18% kieselguhr (dried at 250°) (heated at 275° in vacuo before use)		
<i>n</i> -Butenes	(51.4%)	82% H ₃ PO ₄ (conc. about 89%)	5.40 sec.	275
<i>n</i> -Butane	(48.6%)	+18% kieselguhr (dried at 250°) (heated at 275° in vacuo before use)		
<i>n</i> -Butenes	(51.4%)	82% H ₃ PO ₄ (conc. about 89%)	3.70 sec.	275
<i>n</i> -Butane	(48.6%)	+18% kieselguhr (dried at 250°) (heated at 275° in vacuo before use)		
<i>n</i> -Butenes	(51.4%)	82% H ₃ PO ₄ (conc. about 89%)	43.6 sec.	325
<i>n</i> -Butane	(48.6%)	+18% kieselguhr (dried at 250°) (heated at 325° in vacuo before use)		
<i>n</i> -Butenes	(51.4%)	82% H ₃ PO ₄ (conc. about 89%)	10.8 sec.	325
<i>n</i> -Butane	(48.6%)	+18% kieselguhr (dried at 250°) (heated at 325° in vacuo before use)		
<i>n</i> -Butenes	(51.4%)	82% H ₃ PO ₄ (conc. about 89%)	5.00 sec.	325
<i>n</i> -Butane	(48.6%)	+18% kieselguhr (dried at 250°) (heated at 325° in vacuo before use)		
<i>n</i> -Butenes	(51.4%)	82% H ₃ PO ₄ (conc. about 89%)	2.05 sec.	325
<i>n</i> -Butane	(48.6%)	+18% kieselguhr (dried at 250°) (heated at 325° in vacuo before use)		
<i>n</i> -Butenes	(97%)	82% H ₃ PO ₄ (conc. about 89%)	29.9–31.7 sec.	225
Isobutene	(3%)	+18% kieselguhr (dried at 250°)	27.6 sec.	250
		Steam (equimolar with butenes)	26.8–28.2 sec.	275
			10.2–25.3 sec.	325
<i>n</i> -Butenes	(96–98%)	H ₃ PO ₄ on chamotte (dried at 200–400°)		200–400
Isobutene	(2–4%)			
Butene-1	(12.3%)	H ₃ PO ₄ on chamotte	312 sec.	225
<i>cis</i> -Butene-2	(13.2%)	Steam		
<i>trans</i> -Butene-2	(20.0%)			
Isobutene	(54.5%)			
Butene-1	(14.0%)	H ₃ PO ₄ on chamotte	219 sec.	294
<i>cis</i> -Butene-2	(15.0%)	Steam		
<i>trans</i> -Butene-2	(22.8%)			
Isobutene	(48.2%)			
Butene-1	(27.0%)	H ₃ PO ₄ on chamotte	224 sec.	294
<i>cis</i> -Butene-2	(29.0%)	Steam		
<i>trans</i> -Butene-2	(44.0%)			
Butene-1	(0.70%)	H ₃ PO ₄ on chamotte	210 sec.	294
<i>cis</i> -Butene-2	(0.75%)	Steam		
<i>trans</i> -Butene-2	(1.14%)			
Isobutene	(97.4%)			
Butene-1	(27.0%)	H ₃ PO ₄ on chamotte	262 sec.	355
<i>cis</i> -Butene-2	(29.0%)	Steam		
<i>trans</i> -Butene-2	(44.0%)			

Pressure (atms.)	Products (Per cent by weight on original alkene)			References
	Isomers		Other Products	
1	Isobutene Isobutene	(9.2%)	Alkenes (gaseous) Polymers	(113%) (421) (609a)
1	Isobutene	(24.3%)	Alkenes (gaseous) Polymers	(58%) (609a)
1	Isobutene	(25.3%)	Alkenes (gaseous) Polymers	(41%) (609a)
1	Isobutene	(23.3%)	Alkenes (gaseous) Polymers	(23%) (609a)
1	Isobutene	(16.2%)	Alkenes (gaseous) Polymers	(42%) (609a)
1	Isobutene	(30.2%)	Alkenes (gaseous) Polymers	(30%) (609a)
1	Isobutene	(32.1%)	Alkenes (gaseous) Polymers	(16%) (609a)
1	Isobutene	(15.6%)	Alkenes (gaseous)	(609a)
1	Isobutene = 0.088–0.069			(609a)
1	n-Butenes = 0.075			
1		0.676–0.413		
1		0.511–0.695		
1	Isobutene	(15–40%)	n-Butenes Polymers	(200)
1			n-Butenes Isobutene Polymers	(15.0%) (14.0%) (67.0%) (540)
1			n-Butenes Isobutene Polymers	(47.4%) (45.6%) (7.0%) (540)
1	Isobutene	(17.4%)	n-Butenes Polymers	(61.6%) (21.0%) (540)
1	n-Butenes	(23.5%)	Isobutene Polymers	(45.5%) (31.0%) (540)
1	Isobutene	(28.6%)	n-Butenes Polymers	(54.4%) (17.0%) (540)

Table 10. Isomeriza

Alkene	Reactants	Catalyst (Per cent by weight on alkene + catalyst)	Contact Time (hours)	Temp. (°C.)
Butene-1	(0.70%)	H ₃ PO ₄ on chamotte	311 sec.	355
cis-Butene-2	(0.75%)	Steam		
trans-Butene-2	(1.14%)			
Isobutene	(97.4%)		317 sec.	355
Butene-1	(10.8%)	H ₃ PO ₄ on chamotte		
cis-Butene-2	(11.6%)	Steam		
trans-Butene-2	(17.6%)			
Isobutene	(60.0%)		120-250 sec.	400-500
"Isomerization is effected between isobutene and its normal isomers"		Zeolite		
Isobutene		H ₃ PO ₄ on chamotte (dried at 200-400°)		200-400
		Steam, N ₂ , or CO ₂ (as diluent to reduce polymerization)		
Isobutene		H ₃ PO ₄ + silicate (dried 2-3 hours at 280-300°)	210 sec.	294
		Steam		
Isobutene		H ₃ PO ₄ + silicate (dried 2-3 hours at 280-300°)	246 sec.	294
		Steam		
Pentene-1			8-22 sec.	550-600
Pentene-1		Activated Al ₂ O ₃ (Grade A, 8-14 mesh, Aluminum Ore Co.)	10 passes in 12 hours	357
Pentene-1		Activated SiO ₂ -Al ₂ O ₃	150 g. feed per 100 cc. catalyst per 0.75 hour	400
Pentene-1		100 SiO ₂ + 5Al ₂ O ₃ + 0.5 ThO ₂ (prepared by dehydrating the mixed hydrates at 482°)	3 cc. liquid feed per cc. catalyst per hour	399
Pentene-2			8-22 sec.	550-600
Pentene-2		Xylene (solvent)	8 or 16	100
Pentene-2		Irradiated by Mazda lamp Xylene (solvent)	8	50-60
Pentene-2		Irradiated by Mazda lamp	8	80-90
Pentene-2		Irradiated by Mazda lamp Xylene (solvent)	8	90-100
Pentene-2		Irradiated by Mazda lamp Xylene (solvent)	14.5	145-160

tion of Alkenes—Continued

Pressure (atms.)	Products (Per cent by weight on original alkene)				Refer- ences
	Isomers	Other Products			
1	<i>n</i> -Butenes	(34.7%)	Isobutene Polymers	(38.3%) (27.0%)	(540)
1	<i>n</i> -Butenes	(44.0%)	Isobutene Polymers	(40.0%) (16.0%)	(540)
vapor phase	See Canadian Patent 388,423 for further details				(257)
1	<i>n</i> -Butenes	(up to 40%)	Polymers	(4%)	(200)
1	<i>n</i> -Butenes	(23.5%)	Isobutene Polymers	(45.5%) (31%)	(199) (200)
1	<i>n</i> -Butenes	(43.3%)	Isobutene Polymers	(26.7%) (30%)	(199) (200)
1	Pentene-2		Pentene-1		(261) (265)
slightly above 1	Pentene-2	(78.3%)	Pentene-1	(21.7%)	(172a)
1	2-Methylbutenes	(59.0%)	H ₂ CH ₄ , C ₂ H ₆ , C ₃ H ₈ fraction C ₂ H ₄ Propene + <i>n</i> -butenes Isobutene C ₄ H ₁₀ fraction C ₅ fraction (additional) C ₆ fraction C ₇ -C ₉ fraction C ₁₀ -C _x fraction	(0.01%) (0.5%) (0.1%) (3.0%) (3.0%) (1.0%) (12.7%) (7.7%) (3.8%) (5.1%)	(158)
1	2-Methylbutenes	(59%)	Gas C ₅ fraction (additional) Higher fractions	(7%) (13%) (17%)	(581a)
1	Pentene-1		Pentene-2		(261) (265)
	Shown by HBr product composition:				(302)
	2-bromopentane	(32%)			
	3-bromopentane	(68%)			
	No change shown by HBr product composition:				(302)
	2-bromopentane	(22%)			
	3-bromopentane	(78%)			
	Shown by HBr product composition:				(302)
	2-bromopentane	(29%)			
	3-bromopentane	(71%)			
	Shown by HBr product composition:				(302)
	2-bromopentane	(32%)			
	3-bromopentane	(68%)			
	Shown by HBr product composition:				(302)
	2-bromopentane	(29%)			
	3-bromopentane	(71%)			

Table 10. Isomeriza

Alkene	Reactants		Contact Time (hours)	Temp. (°C.)
		Catalyst (Per cent by weight on alkene + catalyst)		
Pentene-2		Ultraviolet light	6	
Pentene-2		Ultraviolet light	8	
Pentene-2		Ultraviolet light	16	
Pentene-2		Ultraviolet light	29	
Pentene-2		Ultraviolet light Later, "aging"	29 (irradiation) 2 days ("aging")	
Pentene-2		Activated Al ₂ O ₃ (Grade A, 8-14 mesh, Aluminum Ore Co.)	2.5 passes in 3 hours	266
Pentene-2		Activated Al ₂ O ₃ (Grade A, 8-14 mesh, Aluminum Ore Co.)	10 passes in 12 hours	299
Pentene-2		Activated Al ₂ O ₃ (Grade A, 8-14 mesh, Aluminum Ore Co.)	5 passes in 6 hours	300
Pentene-2		Activated Al ₂ O ₃ (Grade A, 8-14 mesh, Aluminum Ore Co.)	2.5 passes in 3 hours	358
Pentene-2		Activated Al ₂ O ₃ (Grade A, 8-14 mesh, Aluminum Ore Co.)	5 passes in 6 hours	359
Pentene-2		Activated Al ₂ O ₃ (Grade A, 8-14 mesh, Aluminum Ore Co.)	10 passes in 12 hours	358
Pentene-2		Activated Al ₂ O ₃ (Grade A, 8-14 mesh, Aluminum Ore Co.)	15 passes in 18 hours	364
Pentene-2		75% Al ₂ O ₃ + 25% CoO	10 passes in 12 hours	320
Pentene-2		75% Al ₂ O ₃ + 25% CoO	10 passes in 12 hours	375
Pentene-2		75% Al ₂ O ₃ + 25% Cr ₂ O ₃	10 passes in 12 hours	295
Pentene-2		75% Al ₂ O ₃ + 25% Cr ₂ O ₃	10 passes in 12 hours	345
Pentene-2		50% Al ₂ O ₃ + 50% Fe ₂ O ₃	10 passes in 12 hours	295
Pentene-2		50% Al ₂ O ₃ + 50% Fe ₂ O ₃	10 passes in 12 hours	344
Pentene-2		75% Al ₂ O ₃ + 25% MnO	10 passes in 12 hours	301
Pentene-2		75% Al ₂ O ₃ + 25% MnO	10 passes in 12 hours	305
Pentene-2		75% Al ₂ O ₃ + 25% MnO	10 passes in 12 hours	362
Pentene-2		75% Al ₂ O ₃ + 25% MnO	10 passes in 12 hours	366
<i>cis</i> -Pentene-2		Xylene (solvent)	(?)	90-100
<i>cis</i> -Pentene-2		Heated (65 hours)	65	at 70-80
		Sunlight (13 weeks) (consecutively)	13 weeks	at room
<i>cis</i> -Pentene-2		Ultraviolet light	4.5	b.p. (?)
<i>cis</i> -Pentene-2		Ultraviolet light	8.5	b.p. (?)

tion of Alkenes—Continued

Pressure (atms.)	Products (Per cent by weight on original alkene)				Refer- ences (302)
	Isomers	Other Products			
	Shown by HBr product composition:				
	2-bromopentane	(30%)			
	3-bromopentane	(70%)			(302)
	Shown by HBr product composition:				
	2-bromopentane	(38%)			
	3-bromopentane	(62%)			(302)
	Shown by HBr product composition:				
	2-bromopentane	(42%)			
	3-bromopentane	(58%)			(302)
	Shown by HBr product composition:				
	2-bromopentane	(49%)			
	3-bromopentane	(51%)			(302)
	Shown by HBr product composition:				
	2-bromopentane	(38%)			
	3-bromopentane	(62%)			
slightly	Pentene-1	(1.9%)	Pentene-2	(98.1%)	(172a)
above 1					
slightly	Pentene-1	(9.3%)	Pentene-2	(90.7%)	(172a)
above 1					
slightly	Pentene-1	(8.0%)	Pentene-2	(92.0%)	(172a)
above 1					
slightly	Pentene-1	(9.9%)	Pentene-2	(90.1%)	(172a)
above 1					
slightly	Pentene-1	(14.4%)	Pentene-2	(85.6%)	(172a)
above 1					
slightly	Pentene-1	(15.7%)	Pentene-2	(84.3%)	(172a)
above 1					
slightly	Pentene-1	(15.2%)	Pentene-2	(84.8%)	(172a)
above 1					
slightly	Pentene-1	(4.6%)	Pentene-2	(95.4%)	(172a)
above 1					
slightly	Pentene-1	(13.5%)	Pentene-2	(86.5%)	(172a)
above 1					
slightly	Pentene-1	(11.7%)	Pentene-2	(88.3%)	(172a)
above 1					
slightly	Pentene-1	(13.3%)	Pentene-2	(86.7%)	(172a)
above 1					
slightly	Pentene-1	(6.8%)	Pentene-2	(93.2%)	(172a)
above 1					
slightly	Pentene-1	(10.5%)	Pentene-2	(89.5%)	(172a)
above 1					
slightly	Pentene-1	(9.3%)	Pentene-2	(90.7%)	(172a)
above 1					
slightly	Pentene-1	(10.6%)	Pentene-2	(89.4%)	(172a)
above 1					
slightly	Pentene-1	(15.3%)	Pentene-2	(84.7%)	(172a)
above 1					
slightly	Pentene-1	(15.4%)	Pentene-2	(84.6%)	(172a)
above 1					
sealed tube	<i>trans</i> -Pentene-2				(301)
sealed tube	<i>trans</i> -Pentene-2				(545)
1	<i>trans</i> -Pentene-2		<i>cis</i> -Pentene-2		(545)
1	<i>trans</i> -Pentene-2		<i>cis</i> -Pentene-2		(545)

Table 10. Isomeriza

Alkene	Reactants (Per cent by weight on alkene + catalyst)	Catalyst	Contact Time (hours)	Temp. (°C.)
<i>cis</i> -Pentene-2	CH ₃ . CO ₂ H (catalyst)		(?)	room
<i>trans</i> -Pentene-2	Ultraviolet light		8.5	b.p. (?)
<i>trans</i> -Pentene-2	CH ₃ . CO ₂ H (catalyst)		(?)	room
<i>n</i> -Pentenes	Al ₂ O ₃ (calcined)			450
<i>n</i> -Pentenes	Sodium permutite		33 sec.	400
<i>n</i> -Pentenes	Sodium permutite		33 sec.	400
<i>n</i> -Pentenes	Sodium permutite		62 sec.	450
<i>n</i> -Pentenes	Sodium permutite		62 sec.	450
"Amylenes" insoluble as vapors in 68% H ₂ SO ₄	Mixture of metaphosphoric and pyrophosphoric acids on dia- tomaceous earth			200-350
2-Methylbutene-1	Activated Al ₂ O ₃ (Grade A, 8-14 mesh, Aluminum Ore Co.)		10 passes in 12 hours	357
3-Methylbutene-1	Activated Al ₂ O ₃ (Grade A, 8-14 mesh, Aluminum Ore Co.)		20 passes in 24 hours	362
3-Methylbutene-1	Al ₂ O ₃		16 sec.	450
3-Methylbutene-1	Al ₂ O ₃ in Cu or glass tubes			450
3-Methylbutene-1	Al ₂ O ₃ in Cu tube		40 g. feed per 2 hours	525-535
2-Methylbutene-1 }	Al ₂ O ₃ in Cu tube		77 g. feed per 40 min.	540-560
3-Methylbutene-1 }				
3-Methylbutene-1	Siliceous earth in Cu tube			500-505
3-Methylbutene-1	Glass tube			400
3-Methylbutene-1	Glass tube			500
3-Methylbutene-1	Glass tube		25 g. feed per hour	530, 540, or 550
3-Methylbutene-1	Glass tube		38 g. feed per 35 min.	600
3-Methylbutene-1	Aluminum sulfate ("A sample of commercial alum was heated in an iron dish until the water of crystallization was just driven off.")		16 sec.	425
3-Methylbutene-1	H ₃ PO ₄ on pumice		14 sec.	500
3-Methylbutene-1	H ₂ SO ₄ (conc. over 60%?)			30-35 (?)
3-Methylbutene-1 (?)	AlCl ₃ (50%)		5 weeks	0-20
2-Methylbutene-2	Activated Al ₂ O ₃ (Grade A, 8-14 mesh, Aluminum Ore Co.)		20 passes in 24 hours	251
2-Methylbutene-2	Activated Al ₂ O ₃ (Grade A, 8-14 mesh, Aluminum Ore Co.)		2.5 passes in 3 hours	263
2-Methylbutene-2	Activated Al ₂ O ₃ (Grade A, 8-14 mesh, Aluminum Ore Co.)		10 passes in 12 hours	266
2-Methylbutene-2	Activated Al ₂ O ₃ (Grade A, 8-14 mesh, Aluminum Ore Co.)		2.5 passes in 3 hours	300
2-Methylbutene-2	Activated Al ₂ O ₃ (Grade A, 8-14 mesh, Aluminum Ore Co.)		10 passes in 12 hours	300
2-Methylbutene-2	Activated Al ₂ O ₃ (Grade A, 8-14 mesh, Aluminum Ore Co.)		2.5 passes in 3 hours	355
2-Methylbutene-2	Activated Al ₂ O ₃ (Grade A, 8-14 mesh, Aluminum Ore Co.)		5 passes in 6 hours	354
2-Methylbutene-2	Activated Al ₂ O ₃ (Grade A, 8-14 mesh, Aluminum Ore Co.)		10 passes in 12 hours	356
2-Methylbutene-2	Activated Al ₂ O ₃ (Grade A, 8-14 mesh, Aluminum Ore Co.)		15 passes in 18 hours	356
2-Methylbutene-2	Activated Al ₂ O ₃ (Grade A, 8-14 mesh, Aluminum Ore Co.)		10 passes in 12 hours	400

tion of Alkenes—Continued

Pressure (atms.)	Products				Refer- ences
	Isomers	(Per cent by weight on original alkene)		Other Products	
1	<i>trans</i> -Pentene-2	(small %)		<i>cis</i> -Pentene-2	(98)
1	<i>cis</i> -Pentene-2	(small %)		<i>trans</i> -Pentene-2	(544)
1	<i>cis</i> -Pentene-2	(small %)		<i>trans</i> -Pentene-2	(98)
	3-Methylbutene-1	(small %)		<i>n</i> -Pentenes	(33)
	2-Methylbutene-2				
1 (?)	2-Methylbutenes	(about 45%)	Undescribed	(about 55%)	(421a)
1 (?)	2-Methylbutenes				(257a)
	(about 53% by vol. of exit-gas)				
1 (?)	2-Methylbutenes	(about 47%)	Undescribed	(about 53%)	(421a)
1 (?)	2-Methylbutenes				(257a)
	(about 56% by vol. of exit-gas)				
1	"Amylenes" soluble	50% as			(200)
	vapors in 68% H ₂ SO ₄				
slightly above 1 slightly above 1	3-Methylbutene-1	(3.6%)	2-Methylbutene-1	(27.0%)	(172a)
	2-Methylbutene-2	(69.4%)			
	2-Methylbutene-1	(27.6%)	3-Methylbutene-1	(3.8%)	(172a)
	2-Methylbutene-2	(68.6%)			
	2-Methylbutene-2	(10%)	3-Methylbutene-1		(413)
	2-Methylbutene-2	(55%)	3-Methylbutene-1	(37%)	(271)
	2-Methylbutene-2	(66%)	Gas		(271)
	2-Methylbutene-2	(below 80%)			(271)
	2-Methylbutene-2				(271)
	2-Methylbutene-2	(trace)			(271)
	2-Methylbutene-2	(trace)			(271)
	2-Methylbutene-2	(small %)			(271)
	2-Methylbutene-2	(trace)	Gases		(271)
	2-Methylbutene-2	(47%)			(413)
	2-Methylbutene-2	(29%)			(413)
1	2-Methylbutene-2	(small %)			(413)
1	Methylcyclobutane		Cyclanes resembling lubricating oil		(16)
			A hexane		
slightly above 1	2-Methylbutene-1	(22.6%)	2-Methylbutene-2	(75.6%)	(172a)
slightly above 1	3-Methylbutene-1	(1.8%)			
slightly above 1	2-Methylbutene-1	(17.3%)	2-Methylbutene-2	(82.7%)	(172a)
slightly above 1	3-Methylbutene-1	(0.0%)			
slightly above 1	2-Methylbutene-1	(22.2%)	2-Methylbutene-2	(77.2%)	(172a)
slightly above 1	3-Methylbutene-1	(0.6%)			
slightly above 1	2-Methylbutene-1	(20.0%)	2-Methylbutene-2	(79.4%)	(172a)
slightly above 1	3-Methylbutene-1	(0.6%)			
slightly above 1	2-Methylbutene-1	(25.6%)	2-Methylbutene-2	(71.9%)	(172a)
slightly above 1	3-Methylbutene-1	(2.5%)			
slightly above 1	2-Methylbutene-1	(20.9%)	2-Methylbutene-2	(78.0%)	(172a)
slightly above 1	3-Methylbutene-1	(1.1%)			
slightly above 1	2-Methylbutene-1	(27.7%)	2-Methylbutene-2	(70.4%)	(172a)
slightly above 1	3-Methylbutene-1	(1.8%)			
slightly above 1	2-Methylbutene-1	(27.3%)	2-Methylbutene-2	(69.6%)	(172a)
slightly above 1	3-Methylbutene-1	(3.1%)			
slightly above 1	2-Methylbutene-1	(26.9%)	2-Methylbutene-2	(69.4%)	(172a)
slightly above 1	3-Methylbutene-1	(3.7%)			
slightly above 1	2-Methylbutene-1	(28.2%)	2-Methylbutene-2	(66.8%)	(172a)
slightly above 1	3-Methylbutene-1	(5.0%)			

Table 10. Isomeriza

Alkene	Reactants		Contact Time (hours)	Temp. (°C.)
	Catalyst (Per cent by weight on alkene + catalyst)			
2-Methylbutene-2	Al ₂ O ₃			520-530 or 540-550
2-Methylbutene-2	75% Al ₂ O ₃ + 25% CoO		10 passes in 12 hours	311
2-Methylbutene-2	75% Al ₂ O ₃ + 25% CoO		10 passes in 12 hours	370
2-Methylbutene-2	75% Al ₂ O ₃ + 25% Cr ₂ O ₃		10 passes in 12 hours	294
2-Methylbutene-2	75% Al ₂ O ₃ + 25% Cr ₂ O ₃		10 passes in 12 hours	345
2-Methylbutene-2	50% Al ₂ O ₃ + 50% Fe ₂ O ₃		10 passes in 12 hours	296
2-Methylbutene-2	50% Al ₂ O ₃ + 50% Fe ₂ O ₃		10 passes in 12 hours	347
2-Methylbutene-2	75% Al ₂ O ₃ + 25% MnO		10 passes in 12 hours	300
2-Methylbutene-2	75% Al ₂ O ₃ + 25% MnO		10 passes in 12 hours	310
2-Methylbutene-2	75% Al ₂ O ₃ + 25% MnO		10 passes in 12 hours	361
2-Methylbutene-2	75% Al ₂ O ₃ + 25% MnO		10 passes in 12 hours	363
2-Methylbutene-2	Permutite		33 sec.	400
2-Methylbutene-2 <i>n</i> -Pentenes	(80%) (20%)	Permutite	33 sec.	400
2-Methylbutene-2 <i>n</i> -Pentenes	(60%) (40%)	Permutite	33 sec.	400
Hexene-1	Al ₂ O ₃ Sample A		3.1 cc. feed per 10 g. catalyst per hour	398
Hexene-1	Al ₂ O ₃ Sample B		3.1 cc. feed per 10 g. catalyst per hour	398
Hexene-1	Al ₂ O ₃		11.2 cc. feed per 10 g. catalyst per hour	398
Hexene-1	Al ₂ O ₃		22.5 cc. feed per 10 g. catalyst per hour	398

tion of Alkenes—Continued

Pressure (atms.) "constant"	Isomers	Products (Per cent by weight on original alkene)		Refer- ences (271)
		No isomers	Other Products	
slightly above 1	2-Methylbutene-1	(11.1%)	2-Methylbutene-2	(87.7%) (172a)
slightly above 1	3-Methylbutene-1	(1.2%)		
slightly above 1	2-Methylbutene-1	(25.8%)	2-Methylbutene-2	(68.1%) (172a)
slightly above 1	3-Methylbutene-1	(6.1%)		
slightly above 1	2-Methylbutene-1	(25.1%)	2-Methylbutene-2	(72.4%) (172a)
slightly above 1	3-Methylbutene-1	(2.5%)		
slightly above 1	2-Methylbutene-1	(26.6%)	2-Methylbutene-2	(68.2%) (172a)
slightly above 1	3-Methylbutene-1	(5.2%)		
slightly above 1	2-Methylbutene-1	(26.2%)	2-Methylbutene-2	(72.5%) (172a)
slightly above 1	3-Methylbutene-1	(1.3%)		
slightly above 1	2-Methylbutene-1	(28.5%)	2-Methylbutene-2	(68.2%) (172a)
slightly above 1	3-Methylbutene-1	(3.3%)		
slightly above 1	2-Methylbutene-1	(21.1%)	2-Methylbutene-2	(77.1%) (172a)
slightly above 1	3-Methylbutene-1	(1.8%)		
slightly above 1	2-Methylbutene-1	(21.1%)	2-Methylbutene-2	(77.7%) (172a)
slightly above 1	3-Methylbutene-1	(1.2%)		
slightly above 1	2-Methylbutene-1	(25.9%)	2-Methylbutene-2	(70.0%) (172a)
slightly above 1	3-Methylbutene-1	(4.1%)		
slightly above 1	2-Methylbutene-1	(26.5%)	2-Methylbutene-2	(69.2%) (172a)
slightly above 1	3-Methylbutene-1	(4.3%)		
1	<i>n</i> -Pentenenes	(19%)	2-Methylbutenes Side products	(66%) (529a) (15%)
	$\frac{2\text{-Methylbutenes}}{n\text{-Pentenenes}} = 3.48$			
1	$\frac{2\text{-Methylbutenes}}{n\text{-Pentenenes}} = 4.56$		<i>n</i> -Pentenenes 2-Methylbutenes Side products	(16%) (529a) (73%) (11%)
1	$\frac{2\text{-Methylbutenes}}{n\text{-Pentenenes}} = 2.08$		<i>n</i> -Pentenenes 2-Methylbutenes Side products	(28%) (529a) (58%) (14%)
1	Hexene-3 2-Methylpentene-2 Lower-boiling 3-methyl- pentene-2 Higher-boiling 3-methyl- pentene-2 2-Ethylbutene-1	(11.3%) (27.7%) (9.8%) (5.3%) (38.7%)	Hexene-1 Carbon on catalyst	(5.9%) (220)
1	Hexene-3 2-Methylpentene-2 Lower-boiling 3-methyl- pentene-2 Higher-boiling 3-methyl- pentene-2 2-Ethylbutene-1	(10.6%) (27.9%) (10.2%) (5.2%) (38.3%)	Hexene-1 Carbon on catalyst	(6.3%) (220)
1	Hexene-2 Hexene-3 2-Methylpentene-2 Lower-boiling 3-methyl- pentene-2 Higher-boiling 3-methyl- pentene-2 2-Ethylbutene-1	(2%) (8%) (12%) (36%) (5%) (13%)	Hexene-1	(24%) (220)
1	Lower-boiling 3-methyl- pentene-2 2-Ethylbutene-1	(9.2%) (1.8%)	Hexene-1	(89%) (220)

Table 10. Isomeriza

Alkene	Reactants		Contact Time (hours)	Temp. (°C.)
	Catalyst (Per cent by weight on alkene + catalyst)			
Hexene-1	Al ₂ O ₃		45.5 cc. feed per 10 g. catalyst per hour	398
Hexene-1	ThO ₂		3.12 cc. feed per 10 g. catalyst per hour	398
Hexene-1	MoS ₃	(5%)	1	400
Hexene-1	ZnCl ₂ on pumice (1 : 1)	(total 69%)	1.5	300-325
Hexene-1	H ₃ PO ₄ on pumice (1 : 1)	(55.6%)	4-5	325-350
<i>n</i> -Hexenes	Al ₂ O ₃ (calcined)			400
2-Methylpentene-2	Al ₂ O ₃		3.12 cc. feed per 10 g. catalyst per hour	398
2-Methylpentene-2	ThO ₂		3.12 cc. feed per 10 g. catalyst per hour	398
Lower-boiling 3-methylpentene-2	Al ₂ O ₃		3.12 cc. feed per 10 g. catalyst per hour	398
Lower-boiling 3-methylpentene-2	Al ₂ O ₃		3.12 cc. feed per 10 g. catalyst per hour	440
Lower-boiling 3-methylpentene-2	ThO ₂		3.12 cc. feed per 10 g. catalyst per hour	398
Lower-boiling 3-methylpentene-2	ThO ₂		3.12 cc. feed per 10 g. catalyst per hour	440
2-Ethylbutene-1	ThO ₂		3.12 cc. feed per 10 g. catalyst per hour	398
3,3-Dimethylbutene	P ₂ O ₅ on silica gel			300
3,3-Dimethylbutene	Activated Al ₂ O ₃		20 cc. feed per hour	350
3,3-Dimethylbutene	Al ₂ (SO ₄) ₃		30 cc. feed per hour	275
3,3-Dimethylbutene 2,3-Dimethylbutenes	(large %) (small %) Al ₂ (SO ₄) ₃			280-290
3,3-Dimethylbutene	Sodium permutite		30 sec.	310
3,3-Dimethylbutene	Permutite or phosphoric acid type of catalysts		short	310

Preparation of Alkenes—Continued

[illegible]

Table 10. Isomeriza

Reactants		Contact Time (hours)	Temp. (°C.)
Alkene	Catalyst (Per cent by weight on alkene + catalyst)		
2,3-Dimethylbutene-1	P ₂ O ₅ on silica gel		300
2,3-Dimethylbutene-2	P ₂ O ₅ on silica gel		300
Heptene-1	Al ₂ O ₃	3.12 cc. feed per 10 g. catalyst per hour	398
Heptene-1	BeO	5 g. feed per ? 44.2 cc. of catalyst per hour (re- treated the b.p. 92–95° fraction from the initial product)	450
2-Methylhexene-2	Al ₂ O ₃	3.12 cc. feed per 10 g. catalyst per hour	398
2-Methylhexene-2	ThO ₂	3.12 cc. feed per 10 g. catalyst per hour	398
3-Methylhexene-2	Al ₂ O ₃	3.12 cc. feed per 10 g. catalyst per hour	398
3-Methylhexene-2	Al ₂ O ₃	3.12 cc. feed per 10 g. catalyst per hour	440
3-Methylhexene-2	ThO ₂	3.12 cc. feed per 10 g. catalyst per hour	398
3-Methylhexenc-2	ThO ₂	3.12 cc. feed per 10 g. catalyst per hour	440
2-Ethylpentene-1	ThO ₂	3.12 cc. feed per 10 g. catalyst per hour	398
Octene-1 { Octene-2 {	Quartz tube		295–365
Octene-1 { Octene-2 {	(91.7%) Glass tube used	836 min.	345
Isooctenes Octene-1 { Octene-2 {	(8.3%) (91.7%) Glass tube used	1.50	380
Isooctenes Octene-1 { Octene-2 {	(8.3%) (91.7%) Glass tube used	2.95	380
Isooctenes Octene-1 { Octene-2 {	(8.3%) (91.7%) Glass tube used	5.75	380
Isooctenes Octene-1 { Octene-2 {	(8.3%) ZnCl ₂ (21.7%)	1.5	300–325

Index of Authors—Continued

[illegible][illegible][illegible][illegible][illegible]

2000-01-01 to 2000-01-01

[illegible]

2010-2011

[illegible]

	(259)	(197)	(259)	(197)	(259)	(197)
genes	186%	genes	186%	genes	186%	genes

Table 10. Isomeriza

Alkene	Reactants		Contact Time (hours)	Temp. (°C.)
	Catalyst (Per cent by weight on alkene + catalyst)			
Octene-1}	ZnCl ₂ on pumice (1 : 1)		25	325-350
Octene-2}	(total 45.5%)			
Octene-1}	ZnCl ₂ on pumice (1 : 1)		25	325-350
Octene-2}	(total 45.5%)			
	Steam			
Octene-1}	ZnCl ₂ on pumice (1 : 1)		13	325-350
Octene-2}	(total 73.5%)			
Octene-1}	Reused-ZnCl ₂ on pumice (1 : 1)		13	325-350
Octene-2}	(total 73.5%)			
Octene-1}	ZnCl ₂ on pumice (1 : 1)		0.50	300-325
Octene-2}	(total 70.8%)			
Octene-1}	ZnCl ₂ on pumice (1 : 1)		1	300-325
Octene-2}	(total 70.8%)			
Octene-1}	ZnCl ₂ on pumice (1 : 1)		1.5	300-325
Octene-2}	(total 67.6%)			
Octene-1}	ZnCl ₂ on pumice (1 : 1)		1.5	300-325
Octene-2}	(total 70.8%)			
Octene-1}	H ₃ PO ₄ on pumice (1 : 1)		1.5	400
Octene-2}	(total 65.2%)			
Octene-1}	Activated SiO ₂ -Al ₂ O ₃		720 g. feed per per 100 cc. catalyst per 2.45 hours	375
Octene-2}				
			</	

Table 10. Isomeriza

Alkene	Reactants		Contact Time (hours)	Temp. (°C.)
	(Per cent by weight on alkene + catalyst)	Catalyst		
Hexadecene (<i>Continued</i>)				
Hexadecene	Activated SiO ₂ -Al ₂ O ₃		1270 g. feed per 100 cc. catalyst per 4.0 hours	400
Hexadecene	Activated SiO ₂ -Al ₂ O ₃		885 g. feed per 100 cc. cata- lyst per 2.78 hours	450
Alkenes	H ₃ PO ₄ or neutral sulfates or phos- phates of metals of the first, second, or third group or of Fe, Co, Ni, Cr, or Mn on a carrier			200-400
Alkenes	Hydrated aluminum silicate hav- ing base-change properties			275-500

Products

Pressure (atms.)	Products (Per cent by weight on original alkene)			Refer- ences	
	Isomers		Other Products		
1	Isohexadecenes	(26.9%)	C ₅ -C ₁₅ fraction (5.7%)	(158)	
			Hexadecene and heavier (47.5%)		
			C ₂ H ₄ (0.1%)		
			C ₂ H ₆ (0.02%)		
			C ₃ H ₆ (1.0%)		
			C ₃ H ₈ (0.08%)		
			<i>n</i> -Butenes (1.4%)		
			Isobutene (1.4%)		
			C ₄ H ₁₀ fraction (0.5%)		
			C ₅ -C ₁₅ fraction (48.8%)		
1	Isohexadecenes	(13.0%)	Hexadecene and heavier (18.3%)	(158)	
			C ₃ H ₆ (3.8%)		
			C ₃ H ₈ (0.4%)		
			<i>n</i> -Butenes (4.6%)		
			Isobutene (4.2%)		
			C ₄ H ₁₀ fraction (1.1%)		
			C ₅ -C ₁₅ fraction (67.5%)		
			Hexadecene and heavier (1.1%)		(200)
			Isomers		
					Isomers

Table 11. Isomerization

Allenic Alkadiene	Reactants		Contact Time (hours)	Temp. (°C.)
	Catalyst (Per cent by weight on alkadiene + catalyst)			
Propadiene	Na Ether (solvent)	(9%) (83%)	24	100
Propadiene	"Floridin"		10.0 cc. feed per 26.5 cc. catalyst per min.	167
Propadiene	"Floridin"		12.0 cc. feed per 26.5 cc. catalyst per min.	220
Propadiene	"Floridin"		10.0 cc. feed per 26.5 cc. catalyst per min.	230
Propadiene	"Floridin"		10.1 cc. feed per 26.5 cc. catalyst per min.	250
Propadiene	"Floridin"		10.7 cc. feed per 26.5 cc. catalyst per min.	270
Propadiene	"Floridin"		8.3 cc. feed per 26.5 cc. cata- lyst per min.	286
Propadiene	"Floridin"		10.0 cc. feed per 26.5 cc. catalyst per min.	312
Propadiene	"Floridin"		5.0 cc. feed per 26.5 cc. cata- lyst per min.	325
Propadiene	"Floridin"		5.0 cc. feed per 26.5 cc. cata- lyst per min.	345
Propadiene	"Floridin"		8.3 cc. feed per 26.5 cc. cata- lyst per min.	350
Propadiene	Alcoholic potash		12	160–170
Butadiene-1,2	Na Ether (solvent)		10 (?)	heated
Butadiene-1,2	"Floridin"			245–330
Butadiene-1,2	Alcoholic potash		9	170
Pentadiene-1,2	NaNH ₂ "Vaseline"		2	140
	Xylene (?) or petroleum (b.p. above 180°) (?)			
3-Methylbutadiene-1,2			2–20 days	100–225

of Allenic Alkadienes

Pressure (atms.) sealed tube	Products (Per cent by weight on original alkadiene)		Refer- ences (239)
	Isomers	Other Products	
	Propyne (Na derivative)		(552)
1	$\frac{\text{Propyne}}{\text{Propadiene}} = 0.1806$		
1	$\frac{\text{Propyne}}{\text{Propadiene}} = 0.2438$	Polymers (6.25%)	(552)
1	$\frac{\text{Propyne}}{\text{Propadiene}} = 0.3263$	Polymers (18.0%)	(552)
1	$\frac{\text{Propyne}}{\text{Propadiene}} = 0.4493$	Polymers (20.0%)	(552)
1	$\frac{\text{Propyne}}{\text{Propadiene}} = 0.7857$	Polymers (37.5%)	(552)
1	$\frac{\text{Propyne}}{\text{Propadiene}} = 0.8692$	Polymers (46.0%)	(552)
1	$\frac{\text{Propyne}}{\text{Propadiene}} = 1.237$	Polymers (58.3%)	(552)
1	$\frac{\text{Propyne}}{\text{Propadiene}} = 1.597$	Polymers (60.0%)	(552)
1	$\frac{\text{Propyne}}{\text{Propadiene}} = 0.5175$	Polymers (65.0%)	(552)
1	$\frac{\text{Propyne}}{\text{Propadiene}} = 0.5038$	Polymers (66.7%)	(552)
	Propyne	Propadiene	(179)
	Butyne-1 (Na derivative)	Ethyl isopropenyl ether	(292)
	Butyne-1 (3.4%)	Butene	(549)
	Butadiene-1,2 (trace)		(292)
1	Butyne-2		(79)
	Pentyne-1 (Na derivative) (large %)	NH ₃ (off at 100–120°)	
bomb tube	2-Methylbutadiene-1,3 (small %)	1,2-Diisopropylidenecyclobutane 1,1-Dimethyl-2-methylene-3-isopropylidenecyclobutane Dipentene	(330)

Table 11. Isomerization

Allenic Alkadiene	Reactants (Per cent by weight on alkadiene + catalyst)	Contact Time (hours)	Temp. (°C.)
3-Methylbutadiene-1,2	Catalyst Activated "Floridin"	0.26 g. feed per min.	215
3-Methylbutadiene-1,2	Activated "Floridin"	0.23 g. feed per min.	232
3-Methylbutadiene-1,2	Activated "Floridin"	0.23 g. feed per min.	280
3-Methylbutadiene-1,2	Activated "Floridin"	0.3 g. feed per min.	334
3-Methylbutadiene-1,2	Na		100
3-Methylbutadiene-1,2	Quinoline hydrobromide (15–20% solution) Quinoline (solvent) Al metal or Al compounds	10–12	130–135
3-Methylbutadiene-1,2	Al ₂ O ₃		heated 300
3-Methylbutadiene-1,2	Al ₂ O ₃		300
Heptadiene-1,2	NaNH ₂ "Vaseline" Xylene (?) or petroleum (b.p. above 180°) (?)	2	140
5-Methylhexadiene-1,2	NaNH ₂ "Vaseline" Xylene (?) or petroleum (b.p. above 180°) (?)	2	140
4,4-Dimethylpentadiene-1,2	Na		heated
4,4-Dimethylpentadiene-1,2	"Floridin"		230–235
2,4-Dimethylpentadiene-2,3		5 days	150
2,4-Dimethylpentadiene-2,3	"Floridin"	0.1–0.15 g. feed per 7.54 cc. catalyst per min.	120
2,4-Dimethylpentadiene-2,3 (94.9%)	"Floridin"	0.1–0.15 g. feed per 7.54 cc. catalyst per min.	170
2,4-Dimethylpentadiene-1,3 (5.1%)			
2,4-Dimethylpentadiene-2,3 (93.3%)	"Floridin"	0.1–0.15 g. feed per 7.54 cc. catalyst per min.	202
2,4-Dimethylpentadiene-1,3 (6.7%)			
2,4-Dimethylpentadiene-2,3	"Floridin"	0.1–0.15 g. feed per 7.54 cc. catalyst per min.	204
2,4-Dimethylpentadiene-2,3 (73.0%)	"Floridin"	0.1–0.15 g. feed per 7.54 cc.	205

Table 12. Isomerization of

Reactants		Contact Time (hours)	Temp. (°C.)
Non-Allenic Alkadiene	Catalyst (Per cent by weight on alkadiene+catalyst)		
Hexadiene-1,4	Concentrated alcoholic potash (Used 4 to 5 volumes of this reagent per 1 volume of hexadiene-1,4)	6	100
Hexadiene-1,5		10 days	250
Hexadiene-1,5	Pyrex-glass tube	13 sec.	500
Hexadiene-1,5	30% Pd+70% asbestos	(1 pass)	200
Hexadiene-1,5	30% Pd+70% C	(2 passes)	200, 300
Hexadiene-1,5	Al ₂ O ₃		300
Hexadiene-1,5	Al ₂ O ₃		360
Hexadiene-1,5	Al ₂ O ₃	15 drops feed per 92.4 cc. catalyst per min.	365
Hexadiene-1,5	Cr ₂ O ₃	0.02 g. liquid feed per "A" 12 cc. catalyst "B" 24 cc. catalyst "C" 35 cc. catalyst "D" 47 cc. catalyst per minute (catalyst col- umn length study, using "A" 15 cm. catalyst "B" 30 cm. catalyst "C" 45 cm. catalyst "D" 60 cm. catalyst)	225 (all cases)
Hexadiene-1,5	Cr ₂ O ₃	"A" 0.02 g. liquid feed "B" 0.05 g. liquid feed "C" 0.10 g. liquid feed "D" 0.20 g. liquid feed "E" 0.40 g. liquid feed per 35 cc. catalyst per minute (feed velocity study)	225 (all cases)

[illegible]

(b) (5), (c)(5); (b) (5), (d)(5); (b) (5), (e)(5); (b) (5), (f)(5)

Table 12. Isomerization of

Non-Allenic Alkadiene	Reactants	Catalyst (Per cent by weight on alkadiene + catalyst)	Contact Time (hours)	Temp. (°C.)
Hexadiene-1,5	Cr ₂ O ₃		0.10 g. liquid feed per 35 cc. catalyst per minute	"A" 225 "B" 250 "C" 275 "D" 300 (tempera- ture effect study)
Hexadiene-1,5	"Floridin"		(6 passes)	225
Hexadiene-1,5	Alcoholic potash		6	170
Hexadiene-2,4	Al ₂ O ₃			360
Hexadiene-2,4	Al ₂ O ₃			450-480
Heptadiene-1,5	Al ₂ O ₃		15 drops feed per 92.4 cc. catalyst per min. (1 pass)	365
2-Methylhexadiene-1,5	Al ₂ O ₃		15 drops feed per 92.4 cc. catalyst per min. (1 pass)	365
3-Methylhexadiene-1,5	Al ₂ O ₃		15 drops feed per 92.4 cc. catalyst per min. (1 pass)	365
2,4-Dimethylpentadiene-1,3 (5.1%)	"Floridin"		0.1-0.15 g. feed per 7.54 cc. catalyst per min.	170
2,4-Dimethylpentadiene-2,3 (94.9%)				
2,4-Dimethylpentadiene-1,3 (6.7%)	"Floridin"		0.1-0.15 g. feed per 7.54 cc. catalyst per min.	202
2,4-Dimethylpentadiene-2,3 (93.3%)				
2,4-Dimethylpentadiene-1,3	"Floridin"		0.1-0.15 g. feed per 7.54 cc. catalyst per min.	204
2,4-Dimethylpentadiene-1,3 (27.0%)	"Floridin"		0.1-0.15 g. feed per 7.54 cc. catalyst per min.	205
2,4-Dimethylpentadiene-2,3 (73.0%)				
2,4-Dimethylpentadiene-1,3 (6.7%)	"Floridin"		0.1-0.15 g. feed per 7.54 cc. catalyst per min.	206
2,4-Dimethylpentadiene-2,3 (93.3%)				
2,4-Dimethylpentadiene-1,3	"Floridin"			230-235
Octadiene-2,6	Al ₂ O ₃		15 drops feed per 92.4 cc. catalyst per min. (1 pass)	365
3-Methylheptadiene-1,5	Al ₂ O ₃		15 drops feed per 92.4 cc. catalyst per min. (1 pass)	365

Non-Allenic Alkadienes—Continued

Pressure (atms.)	Products				Refer- ences
	(Per cent by weight on original alkadiene)		Other Products		
1 (CO ₂)	Hexadiene-2,4	Isomers	"A" (54.0%) "B" (58.2%) "C" (60.9%) "D" (46.7%)	Gases "A" (27%) Gases "B" (18%) Gases and polymers "C" (30%) Gases and polymers "D" (45%) Hexadiene-1,5 "A" (19.0%) "B" (23.8%) "C" (9.1%) "D" (8.3%)	(343)
	Hexadiene-2,4	(41.5%)	Hexadiene-1,5		(333)
	Hexadiene-2,4				(179)
	Hexyne-3 (?)		Hexadiene-2,4	(83%)	(445)
	Hexadiene-1,3	(15%)	Pentadiene-1,3	(8%)	(445)
	Hexadiene-1,4	(2%)	Hexadiene-2,4	(45%)	(593a)
	Hexadiene-1,3	(15%)	Low-boiling hydrocarbons	(small %)	
	Hexadiene-1,4	(20%)	Heptadiene-1,5	(58%)	
	Heptadiene-2,4	(6%)			
	3-Methylhexadiene-1,5	(8%)			
1	2-Methylhexadiene-2,4	(58%)	Low-boiling hydrocarbons	(small %)	(593a)
	4-Methylhexadiene-1,4 or else 2-Ethylpentadiene-1,4	(18%)	Low-boiling hydrocarbons	(small %)	(593a)
	4-Methylhexadiene-1,3 or else 3-Methylhexadiene-2,4	(14%)	2,4-Dimethylpentadiene-1,3	(1.5%)	(551)
			2,4-Dimethylpentadiene-2,3	(68.5%)	
			Polymers	(30%)	(551)
			2,4-Dimethylpentadiene-2,3	(80%)	
			Polymers	(20%)	
			2,4-Dimethylpentadiene-1,3	(5.0%)	(551)
			Polymers	(67%)	
			2,4-Dimethylpentadiene-1,3	(3.8%)	(551)
1	2,4-Dimethylpentadiene-2,3	(28.0%)	2,4-Dimethylpentadiene-2,3	(71.2%)	
			Polymers	(25%)	(551)
			2,4-Dimethylpentadiene-2,3	(67%)	
			Polymers	(33%)	
	2,4-Dimethylpentadiene-2,3				(553)
	Octadiene-3,5 (?)	(small %)	Low-boiling hydrocarbons	(small %)	(593a)
			Octadiene-2,6	(72%)	
	3-Methylheptadiene-2,4 or else 5-Methylheptadiene-2,4	(4%)	Low-boiling hydrocarbons	(small %)	(593a)
			3-Methylheptadiene-1,5	(70%)	

Table 12. Isomerization of

Non-Allenic Alkadiene	Reactants (Per cent by weight on alkadiene + catalyst)	Catalyst	Contact Time (hours)	Temp. (°C.)
2,5-Dimethylhexadiene-1,5			12	260
2,5-Dimethylhexadiene-1,5	Steel equipment was used		time of distillation	b.p.
2,5-Dimethylhexadiene-1,5	Al ₂ O ₃		15 drops feed per 92.4 cc. catalyst per min.	200–225
2,5-Dimethylhexadiene-1,5	Al ₂ O ₃			365
2,5-Dimethylhexadiene-1,5	FeCl ₃		(1 pass)	heated
2,5-Dimethylhexadiene-1,5	MgCl ₂			heated
2,5-Dimethylhexadiene-1,5	"Floridin"			205–210
2,5-Dimethylhexadiene-1,5	KOH			heated
2,5-Dimethylhexadiene-1,5	Alcoholic potash		4	180
2,6-Dimethylheptadiene-1,5 (Geraniolene)	H ₂ SO ₄ 60% H ₂ O 40%		4	100
2,6-Dimethylheptadiene-1,5 (Geraniolene)	H ₂ SO ₄ (sp.gr. 1.56)	(91%?)	36	15
2,6-Dimethylheptadiene-1,5 (Geraniolene)	H ₂ SO ₄ 65% H ₂ O 35%		3 days	room
2,6-Dimethyloctadiene-2,6 (Linaloolene)	H ₂ SO ₄		20 min.	100
2,6-Dimethyloctadiene-2,6 (Dihydromyrcene)	H ₂ SO ₄ + CH ₃ CO ₂ H			room
2,6-Dimethyloctadiene-2,6 (Dihydromyrcene)	H ₂ SO ₄ + CH ₃ CO ₂ H			"low"
2,6-Dimethyloctadiene-2,6 (Dihydromyrcene)	"50% H ₂ SO ₄ " CH ₃ CO ₂ H	(5.5%) (63%)	2	40

Non-Allenic Alkadienes—Continued

Pressure (atms.)	Products		Refer- ences
	Isomers (Per cent by weight on original alkadiene)	Other Products	
	2,5-Dimethylhexadiene-2,4 (41%)		(593a)
1	2,5-Dimethylhexadiene-2,4 (small %)	2,5-Dimethylhexadiene-1,5	(593a)
	2,5-Dimethylhexadiene-2,4		(338)
	2,5-Dimethylhexadiene-1,4 (?) (small %)	Low-boiling hydrocarbons (small %)	(593a)
	2,5-Dimethylhexadiene-2,4 (81%)		
	2,5-Dimethylhexadiene-2,4 (28%)		(593a)
	2,5-Dimethylhexadiene-2,4 (39%)		(593a)
	2,5-Dimethylhexadiene-2,4 (70%)		(333)
	2,5-Dimethylhexadiene-2,4 (small %)		(593a)
	2,5-Dimethylhexadiene-2,4	2,5-Dimethylhexadiene-1,5	(179)
	α -Cyclogeraniolene		(583)
	β -Cyclogeraniolene		
1	α -Cyclogeraniolene (large %)		(632)
	β -Cyclogeraniolene (small %)		
1	α -Cyclogeraniolene		(582)
	β -Cyclogeraniolene		
1	1,5,5,6-Tetramethylcyclohexene-1 (Cyclolinaloolene)		(531)
1	1,5,5,6-Tetramethylcyclohexene-1 (Cyclodihydromyrcene)		(532)
1	1,5,5,6-Tetramethylcyclohexene-1 (Cyclodihydromyrcene) (60–65%)	Dihydrolinalyl acetate (32–33.5%)	(515)
1	1,5,5,6-Tetramethylcyclohexene-1 ("α-Cyclomethylgeraniolene")		(147)

Table 13. Isomeriza

Alkapolyene	Reactants (Per cent by weight on alkapolyene + catalyst)	Catalyst	Contact Time (hours)	Temp. (°C.)
6-Methylheptatriene-1,2,3	K		6	110-120
2,6-Dimethyloctatriene-1,5,7 (Ocimene)			4	b.p.
2,6-Dimethyloctatriene-2,4,6 (Allo-ocimene)	H ₂ SO ₄ + CH ₃ . CO ₂ H			
2,6-Dimethyloctatriene-2,4,6 (Allo-ocimene)			1 0.5 4	250-300 320 300
3-Methylene-7-methyloctadiene- 1,6 (Myrcene)				
4,8-Dimethylnonatriene-1,3,7	H ₂ SO ₄ 80% H ₂ O 20%	(83.3%)		
2,6-Dimethylundecatriene-2,5,8 (Pseudoionane)	H ₂ SO ₄ 2.5% CH ₃ . CO ₂ H 97.5%			b.p.
3,7,11-Trimethyldodecatetraene- 1,3,6,10 (?) (α-Farnesene)	H . CO ₂ H			room (?)
3-Methylene-7,11-dimethyldo- decatriene-1,6,10 (β-Farnesene) +	H . CO ₂ H 90% H ₂ O 10%	(74.3%)	10 min.	120
3,7,11-Trimethyldodecatetra- ene-1,3,6,10 (α-Farnesene)				
3-Methylene-7,11-dimethyldo- decatriene-1,6,10 (β-Farnesene) +	H ₂ SO ₄ 0.5-1.2% CH ₃ . CO ₂ H 98.8-99.5%	(78.4-79.4%)	87	room
3,7,11-Trimethyldodecatetraene- 1,3,6,10 (α-Farnesene)				
2,6,10,15,19,23-Hexamethyltetra- cosaheptaene-2,6,10,14,18,22 (Squalene)	H . CO ₂ H 98% H ₂ O 2%		0.5 3 3 days	b.p. b.p. b.p.
2,6,10,15,19,23-Hexamethyltetra- cosaheptaene-2,6,10,14,18,22 (Squalene)	H ₂ SO ₄ + acetic anhydride		2.5	b.p.
2,6,10,15,19,23-Hexamethyltetra- cosaheptaene-2,6,10,14,18,22 (Squalene)	H ₂ SO ₄ + C ₂ H ₅ OH		18	b.p.
2,6,10,14,19,23,27,31-Octamethyl- dotriacontatridecaene-2,6,8,10, 12,14,16,18,20,22,24,26,30 (Lycopene)	Benzene solution, or Petroleum ether solution		few days (or sooner if heated)	room (or heated)
2,6,10,14,19,23,27,31-Octamethyl- dotriacontatridecaene-2,6,8,10, 12,14,16,18,20,22,24,26,30 (Lycopene)	Benzene (solvent)		1-2 days	20
2,6,10,14,19,23,27,31-Octamethyl- dotriacontatridecaene-2,6,8,10, 12,14,16,18,20,22,24,26,30 (Lycopene)	Benzene (solvent) (almost 100%)		20 min.	b.p.
2,6,10,14,19,23,27,31-Octamethyl- dotriacontatridecaene-2,6,8,10, 12,14,16,18,20,22,24,26,30 (Lycopene)	Benzene (solvent) (almost 100%)		0.5	b.p.

tion of Alkapolyenes

Pressure (atms.) bomb tube	Products		Refer- ences
	Isomers	Other Products	
	(Per cent by weight on original alkapolyene)		
	6-Methylhepten-3-yne-1 (K de- rivative)	H ₂	(227)
1	2,6-Dimethyloctatriene-2,4,6 (Allo-ocimene) (82%)		(167)
(CO ₂)	2,6-Dimethyloctatriene-1,5,7 (Ocimene) (10%)	Polymers	(167)
1	Isomeric terpene	Polymers (38%)	(169)
1	Cyclomyrcene (?)	Polymyrcenes	(8)
1	1,5-Dimethyl-5-allylcyclohexene-1		(243)
1	1,5,5-Trimethyl-6-(1-butenyl)- cyclohexene-1 (α -Ionane)		(226)
1	d- α -Bisabolene (?)		(304)
1 (?)	d- β -Bisabolene (?)		(539)
1	α -Bisabolene (?) } β -Bisabolene (?) } (54.5%)		(482)
1	Hexahydrocadalene	α -Bisabolyl acetate	(486)
1	"Dicyclosqualene"		(244)
1	"Tricyclosqualene"		
1	"Tetracyclosqualene" (respectively)		
1	"Dicyclosqualene" (?)		(244)
1	"Tricyclosqualene" (?)		(244)
1	Neolycopene	Lycopene	(660)
1	Neolycopene (3%)	Lycopene (97%)	(660)
1	Neolycopene	Lycopene	(660)
1	Neolycopene	Lycopene	(661)

Table 13. Isomerization Table 13. Isomerization Table 13. Isomerization

Reactants				Reactants				Reactants			
Conc	Catal	Time	Temp.	Conc	Catal	Time	Temp.	Conc	Catal	Time	Temp.
0.1	0.01	10	140	0.1	0.01	10	140	0.1	0.01	10	140
7,31-Octadec-2,6,8,10,12,14,16,18,20,22,24,26,30	(Lycopene)			7,31-Octadec-2,6,8,10,12,14,16,18,20,22,24,26,30	(Lycopene)			7,31-Octadec-2,6,8,10,12,14,16,18,20,22,24,26,30	(Lycopene)		
2.0				2.0				2.0			
(velocity study)				(velocity study)				(velocity study)			
7,31-Octadec-2,6,8,10,12,14,16,18,20,22,24,26,30	(Lycopene)			7,31-Octadec-2,6,8,10,12,14,16,18,20,22,24,26,30	(Lycopene)			7,31-Octadec-2,6,8,10,12,14,16,18,20,22,24,26,30	(Lycopene)		
(solvent) Neolycopenene				(solvent) Neolycopenene				(solvent) Neolycopenene			
(solvent) Neolycopenene				(solvent) Neolycopenene				(solvent) Neolycopenene			
(solvent) Neolycopenene				(solvent) Neolycopenene				(solvent) Neolycopenene			
5 min				5 min				5 min			
(solvent) Benzene				(solvent) Benzene				(solvent) Benzene			
1.5				1.5				1.5			
(velocity study)				(velocity study)				(velocity study)			

of Alkapolyenes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original alkapolyene)				Refer- ences (661)
	Isomers	Other Products			
1	Neolycopene		Lycopene		
1	Neolycopene	(18%)	Lycopene	(82%)	(661)
1	Neolycopene	(29%)	Lycopene	(71%)	
1	Neolycopene	(43%)	Lycopene	(57%)	
1	Neolycopene	(47%)	Lycopene	(53%)	
1	Neolycopene		Lycopene		(661)
1	Lycopene		Neolycopene		(660)
1	Lycopene		Neolycopene		(660)
1	Lycopene	(6%)	Neolycopene	(94%)	(661)
1	Lycopene	(13%)	Neolycopene	(87%)	(661)
1	Lycopene	(19%)	Neolycopene	(81%)	
1	Lycopene	(30%)	Neolycopene	(70%)	

Table 16. Isomerization of

	Reactants		Contact Time (hours)	Temp. (°C.)
	Alkyne	Catalyst (Per cent by weight on alkyne + catalyst) "Pyrex" glass tube used		
Propyne Nitrogen Oxygen	(95.7%) (3.4%) (0.6%)		74.5 sec.	555
Propyne		"Floridin"	7.0 cc. feed per 26.5 cc. cata- lyst per min.	180
Propyne		"Floridin"	10.4 cc. feed per 26.5 cc. catalyst per min.	231
Propyne		"Floridin"	20.0 cc. feed per 26.5 cc. catalyst per min.	264
Propyne		"Floridin"	10.4 cc. feed per 26.5 cc. catalyst per min.	318
Propyne		"Floridin"	8.0 cc. feed per 26.5 cc. cata- lyst per min.	326
Propyne		"Floridin"	10.0 cc. feed per 26.5 cc. catalyst per min.	348
Propyne		"Floridin"	10.0 cc. feed per 26.5 cc. catalyst per min.	363
Propyne		Alcoholic potash	12	170-180
Butyne-1		"Floridin"		275
Butyne-1		Pumice		300
Butyne-1		Alcoholic potash	16	170
Butyne-1		Alcoholic potash	"few hours"	170-180
Butyne-2		"Floridin"		278
Butyne-2		"Floridin"		280
Butyne-2		"Floridin"		285
Pentyne-1		Alcoholic potash	24	170
Pentyne-1		Alcoholic potash		30 or 40
Pentyne-2		Na (40 mole-per cent)	4-5	100

Pressure (atms.)	Isomers	Products (Per cent by weight on original alkyne)		Refer- ences
		Isomers	Other Products	
740 mm. Hg	Propadiene	(below 13.6%)	CO ₂ (0.37%) CO (0.39%) O ₂ (0.67%) N ₂ (4.27%) H ₂ (0.062%) Alkanes (CH ₄ , etc.; n = 1.67 in C _n H _{2n+2}) (3.5%) Ethylene (0.87%) Propene (?) Propyne (25.8%) Liquids (probably propa- diene polymers) (28%) Polymers (28%)	(370a)
1	$\frac{\text{Propyne}}{\text{Propadiene}} = 4.348$		Polymers (28%)	(552)
1	$\frac{\text{Propyne}}{\text{Propadiene}} = 3.000$		Polymers (30%)	(552)
1	$\frac{\text{Propyne}}{\text{Propadiene}} = 2.484$		Polymers (30%)	(552)
1	$\frac{\text{Propyne}}{\text{Propadiene}} = 1.857$		Polymers (40%)	(552)
1	$\frac{\text{Propyne}}{\text{Propadiene}} = 1.618$		Polymers (43%)	(552)
1	$\frac{\text{Propyne}}{\text{Propadiene}} = 2.030$		Polymers (50%)	(552)
1	$\frac{\text{Propyne}}{\text{Propadiene}} = 1.632$		Polymers (75%)	(552)
	No isomers		Ethyl isopropenyl ether Propyne	(178)
	Butadiene-1,2			(554)
	Butadiene-1,3			(141a)
	Butyne-2		Butyne-1	(176)
	Butyne-2		Butyne-1	(180)
	Butadiene-1,2	(10.8%)		(653)
	Butyne-1	(13.5%)		(554)
	Butadiene-1,2	(36.7%)		(554)
	Butyne-1	(5.1%)		(554)
	Butadiene-1,2	(19.3%)		(176)
	Butyne-1	(14.1%)		(180)
	Pentyne-2			(180)
	Pentyne-2			(180)
	Pentyne-1 (Na derivative)		Pentene-2 (?)	(177)

Table 16. Isomerization of Alkynes,

Reactants		Catalyst (Per cent by weight on alkyne + catalyst)	Contact Time (hours)	Temp. (°C.)
Alkyne				
3-Methylbutyne-1		Alcoholic potash	6	150
3-Methylbutyne-1		Activated "Floridin"	0.4 g. feed per min.	270
3-Methylbutyne-1		Al ₂ O ₃		400
3-Methylbutyne-1		Al ₂ O ₃		heated
3-Methylbutyne-1		Al ₂ O ₃		400
Hexyne-1				500
Hexyne-1				550
Hexyne-1				600
Hexyne-2		Na		150-160
3,3-Dimethylbutyne-1		Alcoholic potash	16	200
Heptyne-1				600
Heptyne-1	(90.0%)	Pumice		350
Heptyne-2	(10.0%)			
Heptyne-1		Alcoholic potash	24	140-150
Heptyne-1		Alcoholic potash	36	140-150
Heptyne-1 (63% pure)		KOH (13.5%)	5	200
		C ₂ H ₅ OH (43.2%)		
Heptyne-1 (76% pure)		Soda-lime	5	275
Heptyne-1	(90.0%)	Soda-lime		380
Heptyne-2	(10.0%)			
Heptyne-1	(20.0%)	NaNH ₂	12	160
Heptyne-2	(80.0%)	Mineral oil (diluent)		
Heptyne-3		NaNH ₂	4	170
		Pseudocumene (diluent)		
Octyne-1		Alcoholic potash	36	140-150
Octyne-2		Na (3.84%)	8	"sand bath"
Octyne-2		Na (16.1%)	(?) and 36	at 100 at "salt bath"
Octyne-2		NaNH ₂	1	150
		Pseudocumene (diluent)		
Octyne-3		NaNH ₂	9	170
		Petroleum (diluent)		
Nonyne-2		NaNH ₂	2	160
		Petroleum (diluent)		
Dodecyne-1		Alcoholic potash		
Dodecyne-2		Na		
Hexadecyne-1		Alcoholic potash		
Hexadecyne-2		Na		
Hexadiyne-1,4		Alcoholic potash	(?)	(?)
Hexadiyne-1,4		Alcoholic potash	1	100
2,2,9,9-Tetramethyl-5,5,6,6-tetra- tert-butylethynyldecadiyne-3,7		Alcohol (solvent) (96-98%)	1	100

Alkadiynes, and Alkapolyynes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original alkyne)		Refer- ences
	Isomers	Other Products	
40–50 mm. Hg reduced 40–50 mm. Hg	3-Methylbutadiene-1,2		(176)
	3-Methylbutadiene-1,2	Polymer	(180)
	$\frac{3\text{-Methylbutyne-1}}{2\text{-Methylbutadiene-1,3}} = 0.08000$	(5%)	(548)
	$\frac{3\text{-Methylbutyne-1}}{2\text{-Methylbutadiene-1,3}} = 0.001081$		
	2-Methylbutadiene-1,3		(639)
	2-Methylbutadiene-1,3		(29)
	2-Methylbutadiene-1,3 (50%)	3-Methylbutyne-1	(32)
	Hexadiene-1,2	Scission products	(263)
	Hexadiene-1,2	Scission products	(263)
	Hexyne-2 (trace)		
No isomers	Hexyne-1 (Na derivative)	C ₆ H ₁₂	(177)
			(176)
	Heptadiene-1,2	Scission products	(263)
	Heptyne-2 (trace)		
	$\frac{\text{Heptyne-1}}{\text{Heptyne-2}} = 2.125$		(234)
	Heptyne-2 (100%)		(42)
	Heptyne-2 (100%)		(41)
	Heptyne-2		(24)
	No isomers		(24)
	Heptyne-1 (13.0%)		(234)
1	Heptyne-2 (65.6%)		
	$\frac{\text{Heptyne-1}}{\text{Heptyne-2}} = \frac{64}{36}$		(234)
	Heptyne-1 (70–80%)		(81)
	Octyne-2 (100%)		(41)
			(42)
	Octyne-1 (9%)	Octyne-2 (large %)	(135)
sealed tube	Octyne-1 (crude, 75%)	Na C ₈ H ₁₆	(43)
	Octyne-1 (80%)		(81)
	Octyne-1 (55%)		(81)
	Nonyne-1 (83%)		(81)
	Dodecyne-2		(323)
	Dodecyne-1		(323)
	Hexadecyne-2		(323)
	Hexadecyne-1		(323)
	Hexadiyne-2,4		(336)
	Hexadiyne-2,4	Hexadiyne-1,5 C ₈ H ₁₂ O Resin	(179)
(?)		(large %)	
	2,2,13,13-Tetramethyl-5,10-di- tert-butylethynyl-7,8,-di-tert- butyltetradecatetraene-5,6,8,9- diyne-3,11 (40–60%)		(499)
sealed tube			

Table 17. Isomerization of Cyclanes and

Cyclane	Reactants Catalyst (Per cent by weight on cyclane + catalyst)	Contact Time (hours)	Temp. (°C.)
Cyclopropane	Glass tube	4000 cc. feed per 1.75 hour 700 cc. feed per 3.25 hours	100
Cyclopropane			"glowing red"
Cyclopropane			360-370
Cyclopropane	"Pyrex" reaction-vessel	8 min.	499.5
Cyclopropane	"Pyrex" reaction-vessel	0.50	499.5
Cyclopropane		20 min.	550
Cyclopropane	Unglazed porcelain tube	27 min.	600
Cyclopropane	Unglazed porcelain tube	51 min.	600
Cyclopropane	Unglazed porcelain tube	54.5 min.	600
Cyclopropane	Unglazed porcelain tube	73 min.	600
Cyclopropane	Glazed porcelain tube, small diameter	31 min.	600
Cyclopropane	Glazed porcelain tube, medium diameter	31 min.	600
Cyclopropane	Glazed porcelain tube, large diameter	31 min.	600
Cyclopropane	Quartz tube	28 min.	600
Cyclopropane	Quartz tube	29 min.	600
Cyclopropane	Quartz tube	43.5 min.	600
Cyclopropane	Al ₂ O ₃	600 cc. feed per 1.75 hour	350-360
Cyclopropane	Al ₂ O ₃		370-385
Cyclopropane	Pt black Air, moisture	5 months	room
Cyclopropane	Pt black Air, moisture	120	100
Cyclopropane	Pt black (Levy's)	700 cc. feed per 1.50 hour	200
Cyclopropane	Pt black (Levy's)	500 cc. feed per 1.75 hour	315
Cyclopropane	Pt asbestos		400
Cyclopropane	Fe filings		600
Cyclopropane	I ₂	18	279.2
Cyclopropane	ZnCl ₂ (anhydrous)	0.5	below b.p. of catalyst

Cyclanes with Saturated Side-Chains

Pressure (atms.)		Products		References
		(Per cent by weight on original cyclane) Isomers	Other Products	
	Propene	(15–18%)		(577)
	Propene	(large %)		(576)
1	Propene	(1–2%)		(279)
37.91 cm. Hg	Propene	(25%)		(104)
37.22 cm. Hg	Propene	(65%)		(104)
1	Propene	(75%)	H ₂ + alkane gas (14% by vol.) C ₂ H ₄ (7% by vol.) Cyclopropane (4%)	(62)
1	Propene	(1.5%)	Cyclopropane (?) Polymer (?)	(590)
1	Propene	(61.5%)	Cyclopropane (?) Polymer (?)	(590)
1	Propene	(70.0%)	Cyclopropane (?) Polymer (?)	(590)
1	Propene	(86.2%)	H ₂ (1.2% by vol.) CH ₄ (1.2% by vol.) Hexene-2 (?)	(590)
1	Propene	(7.9%)	Cyclopropane (?) Polymer (?)	(590)
1	Propene	(16.0%)	Cyclopropane (?) Polymer (?)	(590)
1	Propene	(50.2%)	H ₂ (0.7%? by vol.) CH ₄ (1.4% by vol.) Cyclopropane (?) Polymer (?)	(590)
1	Propene	(76.0%)		(590)
1	Propene	(92.8%)		(590)
1	Propene	(96.5%)		(590)
1	Propene	(15%)		(279)
1	Propene	(20%)		(279)
	Propene	(19–30%)		(577)
	Propene	(45%)		(577)
1	Propene	(4–5%)		(279)
1	Propene	(29%)		(279)
	Propene	(70%)		(472)
	Propene	(50–70%)	Cyclopropane	(270)
				(273)
	Propene	(small %)	CH ₂ I . CH ₂ . CH ₂ I	(426)
Initially: 93.2 mm. Hg (cyclopropane) + 86.6 mm. Hg (iodine vapor) In 3 hours: 144.4 mm. Hg In 18 hours: 177.5 mm. Hg 1	Propene	(40%)	Cyclopropane (60%)	(62)

Table 17. Isomerization of Cyclanes and

	Reactants	Catalyst	Contact Time	Temp.
		(Per cent by weight on cyclane + catalyst)	(hours)	(°C.)
Methylcyclopropane	Al ₂ O ₃		2000 cc. feed per 1.33 hour or 2500 cc. feed per 3 hours or 2450 cc. feed per 3.33 hours or 2240 cc. feed per 3.33 hours	340–356 340–355 350–358 350–360
1,1-Dimethylcyclopropane	Al ₂ O ₃		8 g. feed per 71 min.	340–345
Ethylcyclopropane	Al ₂ O ₃ -asbestos		5 g. feed per 2 hours	300–310
Methylcyclobutane	Al ₂ O ₃		7 g. feed per 2 hours	400
Cyclopentane	AlCl ₃	(23%)	8	b.p.
Methylcyclopentane	Sulfur compounds of Co and of Mo	(15.8%)	1	500
Methylcyclopentane Cyclohexane (various mixtures)	AlBr ₃ + HBr (gas), or AlCl ₃ (partially hydrated)			25.1
Methylcyclopentane Cyclohexane (various mixtures)	AlBr ₃ + HBr (gas), or AlCl ₃ (partially hydrated)		24–48	61.0
Methylcyclopentane Cyclohexane (various mixtures)	AlBr ₃ + HBr (gas), or AlCl ₃ (partially hydrated)			99.5
Methylcyclopentane Cyclohexane	(30%) AlBr ₃ (70%) HBr (gas)	(23.9%) (1.4%)	24	61
Methylcyclopentane	AlCl ₃ HCl (gas)		10	20
Methylcyclopentane	AlCl ₃ (partially hydrated)	(14.0%)	21.5	61
Methylcyclopentane Cyclohexane	(15%) AlCl ₃ (partially (85%) hydrated)	(19.3%)	51	61
Methylcyclopentane	AlCl ₃ H ₂ O	(20.9%) (0.7%)	3	b.p.
Methylcyclopentane	AlCl ₃ HCl (gas)		10	80
Methylcyclopentane	AlCl ₃ HCl (gas)		10	80
Methylcyclopentane	AlCl ₃	(34.6%)	20–22	b.p.
Methylcyclopentane	AlCl ₃ H ₂ O	(30.5%) (0.8%)	30	b.p.

Cyclanes with Saturated Side-Chains—Continued

Pressure (atms.)	Products (Per cent by weight on original cyclane)			Refer- ences
	Isomers	Other Products		
1	Butene-2 Isobutene	(large %) (small %)	Dimer of isobutene (10%)	(140)
1				
1				
1				
1	2-Methylbutene-2	(93.75%)		(279)
1	Pentene-2			(479)
1	2-Methylbutene-1 3-Methylbutene-1 Pentene-2			(480)
1	No isomers		Cyclopentane unchanged	(129)
100 (H ₂)	Cyclohexane	(small %)	Methylcyclopentane (large %)	(452)
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}} = 7.333$ at "equilibrium"			(441)
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}} = 3.651$ at "equilibrium"			(441)
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}} = 1.174$ at "equilibrium"			(441)
sealed tube	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}} = 3.673$			(441)
autoclave	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}} = 8.00$ at "equilibrium"		Low-boiling hydrocarbons (1.0%) Methylcyclopentane (11.0%)	(529a)
sealed tube	Cyclohexane (88.0%) $\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}} = 1.632$			(441)
sealed tube	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}} = 3.651$			(441)
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}} = 2.89$		Low-boiling product (1.8% by volume)	(215)
autoclave	Cyclohexane (58.6%) $\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}} = 3.27$ at "equilibrium"		High-boiling product (9.5% by volume) Methylcyclopentane (23.4%)	(529a)
autoclave	Cyclohexane (76.6%) $\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}} = 3.40$ at "equilibrium"		Low-boiling hydrocarbons (0.6%) Methylcyclopentane (22.5%)	(529a)
1	Cyclohexane (76.5%) $\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}} = 5.25$			(595)
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}} = 3.386$			(399)

Table 17. Isomerization of Cyclanes and

Cyclane	Reactants	Catalyst (Per cent by weight on cyclane + catalyst)	Contact Time (hours)	Temp. (°C.)
1,2-Dimethylcyclopentane	AlCl ₃	(31.2%)		100–104
Ethylcyclopentane	AlCl ₃	(17.3%)	18	50
	H ₂ O	(0.5%)		
Ethylcyclopentane	AlCl ₃	(31.5%)	20	110–115
Propylcyclopentane	AlCl ₃	(16.6%)	18	50
	H ₂ O	(0.4%)		
Propylcyclopentane	AlCl ₃	(28.4%)	20	140–145
Isopropylcyclopentane	AlCl ₃	(15.9%)	18	50
	H ₂ O	(0.4%)		
Isopropylcyclopentane	AlCl ₃	(28.3%)	20 ?	125–130
<i>n</i> -Butylcyclopentane	AlCl ₃	(15.4%)	18	50
	H ₂ O	(0.4%)		
<i>n</i> -Butylcyclopentane	AlCl ₃	(26%)	20–24	160–165
<i>sec</i> -Butylcyclopentane	AlCl ₃	(14.5%)	18	50
	H ₂ O	(0.4%)		
<i>tert</i> -Butylcyclopentane	AlCl ₃	(22.6%)	18	50
	H ₂ O	(0.6%)		
<i>n</i> -Amylcyclopentane	AlCl ₃	(24.1%)	20	150–155
Cyclohexane	Al ₂ O ₃	(6.98%)	4	500–510
Cyclohexane	Al ₂ O ₃ in quartz tube		0.06 g. feed per 28.3 cc. cata- lyst per minute	500
Cyclohexane	Al ₂ O ₃ + ZnCl ₂ in quartz tube		0.06 g. feed per 28.3 cc. cata- lyst per minute	500
Cyclohexane	Al ₂ O ₃ + H ₃ PO ₄ in quartz tube		0.06 g. feed per 28.3 cc. cata- lyst per minute	500
Cyclohexane	BeO			450
Cyclohexane	Quartz tube		0.06–0.1 g. feed (?) per 84.8 cc. reac- tion-space per minute	550
Cyclohexane	TiO ₂			450
Cyclohexane	Copper chromite (Adkins')		0.6 g. feed per 28.3 cc. cata- lyst per minute	500
Cyclohexane	Copper chromite (Adkins')		0.1 g. feed per 28.3 cc. cata- lyst per minute	500

Cyclanes with Saturated Side-Chains—*Continued*

Pressure (atms.)	Products (Per cent by weight on original cyclane)		Refer- ences
	Isomers	Other Products	
1 sealed tube	Methylcyclohexane (96.7%) Methylcyclohexane (90%)		(598c) (440)
sealed tube	Methylcyclohexane (83.4%) 1,3-Dimethylcyclohexane (95.3%)	Ethylcyclopentane (2.6%)	(597) (440)
1 sealed tube	1,3- and 1,4-Dimethyl- cyclohexanes (72.2%) 1,3-Dimethylcyclohexane (96.3%)	Alkanes (1.4%) Propylcyclopentane	(598) (440)
1 sealed tube	1,3- and 1,4-Dimethyl- cyclohexanes (70.2%) 1,3,5-Trimethylcyclohexane (96.4%)	Alkanes Cyclopentane deriva- tives } (17%)	(598a) (440)
1 sealed tube	1,2,4-Trimethylcyclohexane (below 72%) 1,3,5-Trimethylcyclohexane (98%)	Alkanes (5.7%) Cyclopentane deriva- tives (12.3%)	(596) (440)
1 sealed tube	1,3,5-Trimethylcyclohexane (60%)		(440)
1	Tetramethylcyclohexanes (?)	Low-boiling hydrocarbons High-boiling hydrocarbons	(598b)
110–120	Methylcyclopentane (small %)	Hydrogen Methane Other hydrocarbons	(275)
1	Not considered	Gas with 75.04% H ₂ , 2.2% sat- urated hydrocarbons, and 4.1% unsaturated hydrocarbons Catalyzate with 4.2% unsatu- rated hydrocarbons, 66.3% cyclanes, and 29.5% aromatics	(297a)
1	Not considered (The catalyzate had 5.1% of iso-compounds in cyclanes and aromatics.)	Gas with 92.2% H ₂ , 0.0% satu- rated hydrocarbons, and 0.8% unsaturated hydrocarbons Catalyzate with 5.3% unsatu- rated hydrocarbons, 66.2% cyclanes, and 28.5% aromatics	(297a)
1	Not considered (The catalyzate had 5.5% of iso-compounds in alkanes and cyclanes.)	Catalyzate with 3.7% alkanes, 4.3% unsaturated hydrocar- bons, 87.7% cyclanes, and 5.3% aromatics	(297a)
1	No isomers	Cyclohexane (100%)	(12a)
1	No isomers	Cyclohexane (100%)	(297a)
1	No isomers	Cyclohexane (large %) Benzene (small %)	(12a)
1	Not considered (The catalyzate had 2.4% of iso-compounds in alkanes and cyclanes.)	Gas with 96.18% H ₂ Catalyzate with 1.2% alkanes, 2.7% unsaturated hydrocar- bons, 28.8% cyclanes, and 57.3% aromatics	(297a)
1	Not considered (The catalyzate had 2.5% of iso-compounds in alkanes and cyclanes.)	Gas with 95.8% H ₂ Catalyzate with 2.07% alkanes, 2.3% unsaturated hydrocar- bons, 16.94% cyclanes, and 77.7% aromatics	(297a)

Table 17. Isomerization of Cyclanes and

	Reactants	Catalyst	Contact Time	Temp.
		(Per cent by weight on cyclane+catalyst)	(hours)	(°C.)
Cyclohexane		Sulfur compounds of Co and of Mo (15.8%)	1	450
Cyclohexane		Sulfur compounds of Co and of Mo (15.8%)	1	500
Cyclohexane		MoS ₂ (9.0%)	26	400
Cyclohexane		MoS ₂		400
Cyclohexane		MoS ₂		500
Cyclohexane		Molybdenum sulfide <i>via</i> addition of H ₂ SO ₄ to solution of molyb- denum oxide in ammonium sulfide. Supported (1 part) on Japanese acid clay (5 parts) that was prior-activated by mineral acids.	145 cc. feed per 717 cc. cata- lyst per hour	379
Cyclohexane		Molybdenum sulfide <i>via</i> addition of H ₂ SO ₄ to solution of molyb- denum oxide in ammonium sulfide. Supported (1 part) on Japanese acid clay (5 parts) that was prior-activated by mineral acids.	113 cc. feed per 717 cc. cata- lyst per hour	411
Cyclohexane		Molybdenum sulfide <i>via</i> addition of H ₂ SO ₄ to solution of molyb- denum oxide in ammonium sulfide. Supported (1 part) on Japanese acid clay (6 parts) that was prior-activated by mineral acids (24.1%) H ₂ (7.1%)	1	430
Cyclohexane		MoO ₃ (8.2%) Sulfur (1.4%) H ₂ (8.4%)	1	430
Cyclohexane		MoO ₃ (8.2%) Sulfur (1.4%) H ₂ (8.4%)	1	430
Cyclohexane		MoO ₃ (8.1%) Sulfur (1.4%) H ₂ (9.4%)	2	439
Cyclohexane		Potash-glass tube	6-8	300
Cyclohexane		Potash-glass tube	8	330
Cyclohexane		Soda-glass tube	8	330
Cyclohexane		Alkali-glass tube	3 days	350
Cyclohexane		Alkali-glass tube	3 days	420
Cyclohexane		AlBr ₃ (51.4%)	12	180

Cyclanes with Saturated Side-Chains—Continued

Pressure (atms.)	Products				Refer- ences
	Isomers	(Per cent by weight on original cyclane)		Other Products	
100 (H ₂)	Methylcyclopentane	(small %)	Cyclohexane	(large %)	(452)
100 (H ₂)	Methylcyclopentane	(large %)	C ₇ H ₁₄	(small %)	(452)
140–350 (H ₂)	Methylcyclopentane (62% of re- covered hydrocarbons)		Cyclohexane	(small %)	(454)
300? (H ₂)	Methylcyclopentane		<i>n</i> -Hexane		(453b)
300? (H ₂)	Methylcyclopentane		Isohexanes		(453b)
			<i>n</i> -Hexane		
			Isohexanes		
			Gases		
			Isohexanes		
			Unsaturated hydrocarbons		
			Aromatics		
200 (H ₂)	Methylcyclopentane	(33.4%)	Cyclohexane	(60.9%)	(4)
			Unsaturated hydrocarbons	(0.8%)	(5b)
			Aromatics	(0.1%)	
200 (H ₂)	Methylcyclopentane	(67.7%)	Cyclohexane	(17.6%)	(4)
			Unsaturated hydrocarbons	(0.4%)	
			Aromatics	(0.6%)	
242 (H ₂)	Methylcyclopentane	(17.2%)	H ₂ (99.74% was recovered)		(5a)
			Low-boiling fractions	(0.84%)	
			Unsaturated hydrocarbons in 77–81° b.p. fraction	(0.27%)	
			Aromatic hydrocarbons in 77–81° b.p. fraction	(0.18%)	
			Cyclohexane	(72.9%)	
			High-boiling fraction	(0.28%)	
			Distillation residue	(1.5%)	
240 (H ₂)	Methylcyclopentane	(15.3%)	Cyclohexane	(75.8%)	(5)
			Saturated hydrocarbons	(2.6%)	
			Unsaturated hydrocarbons	(0.2%)	
			Aromatics	(0.6%)	
240 (H ₂)	Methylcyclopentane	(15.3%)	H ₂ (99.70% was recovered)		(5a)
			CH ₄	(0.2%)	
			Low-boiling fraction	(0.47%)	
			Unsaturated hydrocarbons in 77–80° b.p. fraction	(0.18%)	
			Aromatic hydrocarbons in 77–80° b.p. fraction	(0.55%)	
			Cyclohexane	(75.8%)	
			High-boiling fraction	(0.95%)	
			Distillation residue	(1.2%)	
262–261 (H ₂)	Methylcyclopentane	(10.9%)	Cyclohexane	(80.5%)	(5)
			Saturated hydrocarbons	(2.4%)	
			Unsaturated hydrocarbons	(0.4%)	
			Aromatics	(0.0%)	
sealed tube	Methylcyclopentane	(small %)	Cyclohexane	(large %)	(16)
sealed tube	Methylcyclopentane	(large %)	Cyclohexane	(large %)	(16)
sealed tube	No isomers		Cyclohexane	(100%)	(16)
sealed tube	No isomers		Cyclohexane	(100%)	(547)
sealed tube	Methylcyclopentane	(5%)	Cyclohexane	(95%)	(547)
	No isomers		"Cyclohexane"		(674)

Table 17. Isomerization of Cyclanes and

	Reactants	Catalyst	Contact Time	Temp.
	(Per cent by weight on cyclane + catalyst)		(hours)	(°C.)
Cyclohexane	AlBr ₃	(51.4%)	24	100
Cyclohexane	AlBr ₃	(24.1%)	3	61
	HBr (gas)	(1.3%)		
Cyclohexane	AlBr ₃	(25.1%)	48	61
	HBr (gas)	(1.5%)		
Cyclohexane	AlCl ₃	(66.7%)	48	at room (then heated to b.p.)
Cyclohexane	AlCl ₃	(28%)	few minutes	at b.p.
Methylcyclopentane (various mixtures)	H ₂ O	(0.9%)	then 3-4 weeks	at 25
Cyclohexane	AlCl ₃ (partially hydrated), or			25.1
Methylcyclopentane (various mixtures)	AlBr ₃ + HBr (gas)			
Cyclohexane	AlCl ₃	(28%)	few minutes	at b.p.
Methylcyclopentane (various mixtures)	H ₂ O	(0.9%)	then 3-4 weeks	at 35
Cyclohexane	AlCl ₃	(28%)	few minutes	at b.p.
Methylcyclopentane (various mixtures)	H ₂ O	(0.9%)	then 3-4 weeks	at 45
Cyclohexane	AlCl ₃	(28%)	few minutes	at b.p.
Methylcyclopentane (various mixtures)	H ₂ O	(0.9%)	then 3-4 weeks	at 55
Cyclohexane	AlCl ₃ (partially hydrated)	(13.7%)	23	61
Cyclohexane	AlCl ₃ (partially hydrated), or		24-48	61.0
Methylcyclopentane (various mixtures)	AlBr ₃ + HBr (gas)			
Cyclohexane	AlCl ₃	(28%)	few minutes	at b.p.
Methylcyclopentane (various mixtures)	H ₂ O	(0.9%)	then 3-4 weeks	at 65
Cyclohexane	AlCl ₃	(29.8%)	3	b.p.
	H ₂ O	(0.8%)		
Cyclohexane	AlCl ₃	(29.8%)	16	b.p.
	H ₂ O	(0.8%)		
Cyclohexane	AlCl ₃	(20.4%)	3	b.p.
	H ₂ O	(0.4%)		
Cyclohexane	AlCl ₃	(20.4%?)	3 (?)	b.p. (?)
	H ₂ O	(0.4%?)		
Cyclohexane	AlCl ₃	(28%)	2	77.4
Methylcyclopentane (various mixtures)	H ₂ O	(0.9%)		99.5
Cyclohexane	AlCl ₃ (partially hydrated), or			
Methylcyclopentane (various mixtures)	AlBr ₃ + HBr (gas)			
Cyclohexane	AlCl ₃		10	110
	HCl (gas)			

Cyclanes with Saturated Side-Chains—*Continued*

Pressure (atms.)	Products (Per cent by weight on original cyclane)		Refer- ences
	Isomers	Other Products	
1	Methylcyclopentane (?)	Alkanes (?)	(675)
	Dimethylcyclobutane (3.57%)	Cyclohexane (?)	
sealed tube	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}} = 7.197$		(441)
sealed tube	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}} = 3.310$		(441)
1	Methylcyclopentane	HCl Cyclohexane Resins (large %)	(16)
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}} = 7.00$		(215)
1	average value at "equilibrium"		
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}} = 7.333$		(441)
	at "equilibrium"		
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}} = 5.90$		(215)
1	average value at "equilibrium"		
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}} = 5.18$		(215)
1	average value at "equilibrium"		
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}} = 4.20$		(215)
1	average value at "equilibrium"		
sealed tube	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}} = 1.462$		(441)
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}} = 3.651$		(441)
	at "equilibrium"		
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}} = 3.67$		(215)
	at "equilibrium"		
1	Methylcyclopentane (below 5%)	Cyclohexane <i>n</i> -Hexane (?)	(399)
1	Methylcyclopentane (20.6%)	Cyclohexane	(643a)
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}} = 3.95$ (?)	Low-boiling product High-boiling product	(215)
1 (?)	Methylcyclopentane (16.0%)	Isohexanes (0.28%) Cyclohexane Methylcyclohexane (0.13%) 1,3-Dimethylcyclohexane (0.16%) Dimethyldicyclopentyl } (0.23%) Dicyclohexyl }	(215)
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}} = 2.91$		(215)
	average value at "equilibrium"		
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}} = 1.174$		(441)
	at "equilibrium"		
autoclave	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}} = 1.86$	Low-boiling hydrocarbons (5.6%) Cyclohexane (59.3%) High-boiling hydrocarbons (3.2%)	(529a)
	at "equilibrium"		
	Methylcyclopentane (31.9%)		

[illegible][illegible]

[illegible]

[Return to the top of the page](#)
[Return to the top of the page](#)
[Return to the top of the page](#)
[Return to the top of the page](#)

[illegible]

Chain Unsaturation Side-Chain Unsaturation Side-Chain Unsaturation Side-Chain Unsaturation

Products	Products	Products	Products
Weight on original product by weight on original product by weight on original product by weight on original product	Weight on original product by weight on original product by weight on original product by weight on original product	Weight on original product by weight on original product by weight on original product by weight on original product	Weight on original product by weight on original product by weight on original product by weight on original product
(Same) Other Products (Same) Other Products (Same) Other Products (Same) Other Products	(Same) Other Products (Same) Other Products (Same) Other Products (Same) Other Products	(Same) Other Products (Same) Other Products (Same) Other Products (Same) Other Products	(Same) Other Products (Same) Other Products (Same) Other Products (Same) Other Products
Diene-1,3 (372) Butadiene-1,3 (372) Butadiene-1,3 (372) Butadiene-1,3 (372)			
Methylcyclobutene (417) 1-Methylcyclobutene (417) 1-Methylcyclobutene (417) 1-Methylcyclobutene (417)			
Methylcyclobutene (239) 1-Methylcyclobutene (239) 1-Methylcyclobutene (239) 1-Methylcyclobutene (239)			
Methylcyclobutene (439) 1-Methylcyclobutene (439) 1-Methylcyclobutene (439) 1-Methylcyclobutene (439)			
Methylcyclobutene (439) 1-Methylcyclobutene (439) 1-Methylcyclobutene (439) 1-Methylcyclobutene (439)			
Methylcyclobutene (672) 1-Methylcyclobutene (672) 1-Methylcyclobutene (672) 1-Methylcyclobutene (672)			
Methylcyclobutene (238) 1-Methylcyclobutene (238) 1-Methylcyclobutene (238) 1-Methylcyclobutene (238)			
Methylcyclobutene (2140) 2-Methylcyclobutene (2140) 2-Methylcyclobutene (2140) 2-Methylcyclobutene (2140)			
p-Cymene Polymers 1 1 1 1			
1 1 1 1			
propylcyclopentene (630) 1-Isopropylcyclopentene (630) 1-Isopropylcyclopentene (630) 1-Isopropylcyclopentene (630)			
Methylcyclohexene (481) (46.1%) Methylcyclohexene (481) (46.1%) Methylcyclohexene (481) (46.1%) Methylcyclohexene (481) (46.1%)			
Methylcyclohexene (181) (71.4%) Methylcyclohexene (181) (71.4%) Methylcyclohexene (181) (71.4%) Methylcyclohexene (181) (71.4%)			
Methylcyclohexene (181) (75.0%) Methylcyclohexene (181) (75.0%) Methylcyclohexene (181) (75.0%) Methylcyclohexene (181) (75.0%)			
Methylcyclohexene (608) 1-Methylcyclohexene (608) 1-Methylcyclohexene (608) 1-Methylcyclohexene (608)			
Methylcyclohexene (628) 1-Methylcyclohexene (628) 1-Methylcyclohexene (628) 1-Methylcyclohexene (628)			
Methylcyclohexene (629) 1-Ethylcyclohexene (629) 1-Ethylcyclohexene (629) 1-Ethylcyclohexene (629)			
Methylcyclohexene (104) 1-Vinylcyclohexene (104) 1-Vinylcyclohexene (104) 1-Vinylcyclohexene (104)			
Methylcyclohexene (160) 1-Vinylcyclohexene (160) 1-Vinylcyclohexene (160) 1-Vinylcyclohexene (160)			
Methylcyclohexene (262) 1-Vinylcyclohexene (262) 1-Vinylcyclohexene (262) 1-Vinylcyclohexene (262)			
propylcyclohexene (638) 1-Isopropylcyclohexene (638) 1-Isopropylcyclohexene (638) 1-Isopropylcyclohexene (638)			
propylcyclohexene (631) 1-Isopropylcyclohexene (631) 1-Isopropylcyclohexene (631) 1-Isopropylcyclohexene (631)			
Methyl-3-isopropylcyclohexene-1 (?) 1-Methyl-3-isopropylcyclohexene-1 (?) 1-Methyl-3-isopropylcyclohexene-1 (?) 1-Methyl-3-isopropylcyclohexene-1 (?)			
Methyl-4-isopropylcyclohexene-1 (?) dl-1-Methyl-4-isopropylcyclohexene-1 (?) dl-1-Methyl-4-isopropylcyclohexene-1 (?) dl-1-Methyl-4-isopropylcyclohexene-1 (?)			

Isomerisation of β -lactams	Isomerisation of α -lactams	Isomerisation of β -lactams
<p>1. β-lactams</p> <p>2. α-lactams</p> <p>3. γ-lactams</p> <p>4. δ-lactams</p> <p>5. ϵ-lactams</p> <p>6. ζ-lactams</p> <p>7. η-lactams</p> <p>8. θ-lactams</p> <p>9. ι-lactams</p> <p>10. κ-lactams</p> <p>11. λ-lactams</p> <p>12. μ-lactams</p> <p>13. ν-lactams</p> <p>14. ξ-lactams</p> <p>15. \omicron-lactams</p> <p>16. π-lactams</p> <p>17. ρ-lactams</p> <p>18. σ-lactams</p> <p>19. τ-lactams</p> <p>20. υ-lactams</p> <p>21. ϕ-lactams</p> <p>22. χ-lactams</p> <p>23. ψ-lactams</p> <p>24. ω-lactams</p> <p>25. ϖ-lactams</p> <p>26. ϱ-lactams</p> <p>27. ς-lactams</p> <p>28. ζ-lactams</p> <p>29. η-lactams</p> <p>30. θ-lactams</p> <p>31. ι-lactams</p> <p>32. κ-lactams</p> <p>33. λ-lactams</p> <p>34. μ-lactams</p> <p>35. ν-lactams</p> <p>36. ξ-lactams</p> <p>37. \omicron-lactams</p> <p>38. π-lactams</p> <p>39. ρ-lactams</p> <p>40. σ-lactams</p> <p>41. τ-lactams</p> <p>42. υ-lactams</p> <p>43. ϕ-lactams</p> <p>44. χ-lactams</p> <p>45. ψ-lactams</p> <p>46. ω-lactams</p> <p>47. ϖ-lactams</p> <p>48. ϱ-lactams</p> <p>49. ς-lactams</p> <p>50. ζ-lactams</p> <p>51. η-lactams</p> <p>52. θ-lactams</p> <p>53. ι-lactams</p> <p>54. κ-lactams</p> <p>55. λ-lactams</p> <p>56. μ-lactams</p> <p>57. ν-lactams</p> <p>58. ξ-lactams</p> <p>59. \omicron-lactams</p> <p>60. π-lactams</p> <p>61. ρ-lactams</p> <p>62. σ-lactams</p> <p>63. τ-lactams</p> <p>64. υ-lactams</p> <p>65. ϕ-lactams</p> <p>66. χ-lactams</p> <p>67. ψ-lactams</p> <p>68. ω-lactams</p> <p>69. ϖ-lactams</p> <p>70. ϱ-lactams</p> <p>71. ς-lactams</p> <p>72. ζ-lactams</p> <p>73. η-lactams</p> <p>74. θ-lactams</p> <p>75. ι-lactams</p> <p>76. κ-lactams</p> <p>77. λ-lactams</p> <p>78. μ-lactams</p> <p>79. ν-lactams</p> <p>80. ξ-lactams</p> <p>81. \omicron-lactams</p> <p>82. π-lactams</p> <p>83. ρ-lactams</p> <p>84. σ-lactams</p> <p>85. τ-lactams</p> <p>86. υ-lactams</p> <p>87. ϕ-lactams</p> <p>88. χ-lactams</p> <p>89. ψ-lactams</p> <p>90. ω-lactams</p> <p>91. ϖ-lactams</p> <p>92. ϱ-lactams</p> <p>93. ς-lactams</p> <p>94. ζ-lactams</p> <p>95. η-lactams</p> <p>96. θ-lactams</p> <p>97. ι-lactams</p> <p>98. κ-lactams</p> <p>99. λ-lactams</p> <p>100. μ-lactams</p> <p>101. ν-lactams</p> <p>102. ξ-lactams</p> <p>103. \omicron-lactams</p> <p>104. π-lactams</p> <p>105. ρ-lactams</p> <p>106. σ-lactams</p> <p>107. τ-lactams</p> <p>108. υ-lactams</p> <p>109. ϕ-lactams</p> <p>110. χ-lactams</p> <p>111. ψ-lactams</p> <p>112. ω-lactams</p> <p>113. ϖ-lactams</p> <p>114. ϱ-lactams</p> <p>115. ς-lactams</p> <p>116. ζ-lactams</p> <p>117. η-lactams</p> <p>118. θ-lactams</p> <p>119. ι-lactams</p> <p>120. κ-lactams</p> <p>121. λ-lactams</p> <p>122. μ-lactams</p> <p>123. ν-lactams</p> <p>124. ξ-lactams</p> <p>125. \omicron-lactams</p> <p>126. π-lactams</p> <p>127. ρ-lactams</p> <p>128. σ-lactams</p> <p>129. τ-lactams</p> <p>130. υ-lactams</p> <p>131. ϕ-lactams</p> <p>132. χ-lactams</p> <p>133. ψ-lactams</p> <p>134. ω-lactams</p> <p>135. ϖ-lactams</p> <p>136. ϱ-lactams</p> <p>137. ς-lactams</p> <p>138. ζ-lactams</p> <p>139. η-lactams</p> <p>140. θ-lactams</p> <p>141. ι-lactams</p> <p>142. κ-lactams</p> <p>143. λ-lactams</p> <p>144. μ-lactams</p> <p>145. ν-lactams</p> <p>146. ξ-lactams</p> <p>147. \omicron-lactams</p> <p>148. π-lactams</p> <p>149. ρ-lactams</p> <p>150. σ-lactams</p> <p>151. τ-lactams</p> <p>152. υ-lactams</p> <p>153. ϕ-lactams</p> <p>154. χ-lactams</p> <p>155. ψ-lactams</p> <p>156. ω-lactams</p> <p>157. ϖ-lactams</p> <p>158. ϱ-lactams</p> <p>159. ς-lactams</p> <p>160. ζ-lactams</p> <p>161. η-lactams</p> <p>162. θ-lactams</p> <p>163. ι-lactams</p> <p>164. κ-lactams</p> <p>165. λ-lactams</p> <p>166. μ-lactams</p> <p>167. ν-lactams</p> <p>168. ξ-lactams</p> <p>169. \omicron-lactams</p> <p>170. π-lactams</p> <p>171. ρ-lactams</p> <p>172. σ-lactams</p> <p>173. τ-lactams</p> <p>174. υ-lactams</p> <p>175. ϕ-lactams</p> <p>176. χ-lactams</p> <p>177. ψ-lactams</p> <p>178. ω-lactams</p> <p>179. ϖ-lactams</p> <p>180. ϱ-lactams</p> <p>181. ς-lactams</p> <p>182. ζ-lactams</p> <p>183. η-lactams</p> <p>184. θ-lactams</p> <p>185. ι-lactams</p> <p>186. κ-lactams</p> <p>187. λ-lactams</p> <p>188. μ-lactams</p> <p>189. ν-lactams</p> <p>190. ξ-lactams</p> <p>191. \omicron-lactams</p> <p>192. π-lactams</p> <p>193. ρ-lactams</p> <p>194. σ-lactams</p> <p>195. τ-lactams</p> <p>196. υ-lactams</p> <p>197. ϕ-lactams</p> <p>198. χ-lactams</p> <p>199. ψ-lactams</p> <p>200. ω-lactams</p> <p>201. ϖ-lactams</p> <p>202. ϱ-lactams</p> <p>203. ς</p>		

Reactants				Reactants				Reactants			
Conc.	Catalytic	Temp.		Conc.	Catalytic	Temp.		Conc.	Catalytic	Temp.	
100%	(100%)	5-Cycl	100%	100%	(100%)	5-Cycl	100%	100%	(100%)	5-Cycl	100%
Pentyn-2	2.5		Pentyn-2	2.5		Pentyn-2	2.5	Pentyn-2	2.5		Pentyn-2
Petroleum (diluent)			Petroleum (diluent)			Petroleum (diluent)		Petroleum (diluent)			Petroleum (diluent)
Hexyn-2	2		Hexyn-2	2		Hexyn-2	2	Hexyn-2	2		Hexyn-2
Petroleum (diluent)			Petroleum (diluent)			Petroleum (diluent)		Petroleum (diluent)			Petroleum (diluent)
Hexyn-22	22		Hexyn-22	22		Hexyn-22	22	Hexyn-22	22		Hexyn-22
Petroleum (diluent)			Petroleum (diluent)			Petroleum (diluent)		Petroleum (diluent)			Petroleum (diluent)

Table 10. Isomeriza

Fountain				Reactor				Reactor			
Conc.	Q	Time	Temp.	Conc.	Q	Time	Temp.	Conc.	Q	Time	Temp.
Hydrochloric acid (10%)	100 ml/min.	100	100°C	Hydrochloric acid (10%)	100 ml/min.	100	100°C	Hydrochloric acid (10%)	100 ml/min.	100	100°C
Hydrochloric acid (10%)	100 ml/min.	100	100°C	Hydrochloric acid (10%)	100 ml/min.	100	100°C	Hydrochloric acid (10%)	100 ml/min.	100	100°C

100 drops per min.	500 drops per min.	1000 drops per min.	5000 drops per min.
Spino[4]thene isomerization without CO ₂ atmosphere)	Spino[4]thene isomerization without CO ₂ atmosphere)	Spino[4]thene isomerization without CO ₂ atmosphere)	Spino[4]thene isomerization without CO ₂ atmosphere)

CHIRALITY - CHIRALITY - CHIRALITY - CHIRALITY

Chain-Continued	Side-Chain-Continued	Side-Chain-Continued	Side-Chain-Continued
Products	Products	Products	Products
light on original	light on original	light on original	light on original
(671e)	(671e)	(671e)	(671e)
olohexylpentene-1	olohexylpentene-1	olohexylpentene-1	olohexylpentene-1
(709)	(709)	(709)	(709)
olohexylpentene-2	olohexylpentene-2	olohexylpentene-2	olohexylpentene-2
(183)	(183)	(183)	(183)
olohexylhexene-1	olohexylhexene-1	olohexylhexene-1	olohexylhexene-1
(91)	(91)	(91)	(91)
olohexylhexene-2	olohexylhexene-2	olohexylhexene-2	olohexylhexene-2
(183)	(183)	(183)	(183)

tion of Spiranes	tion of Spiranes	tion of Spiranes	tion of Spiranes
Products	Products	Products	Products
light on original	light on original	light on original	light on original
(671e)	(671e)	(671e)	(671e)
mer, b.p. 185.5-186	mer, b.p. 185.5-186	mer, b.p. 185.5-186	mer, b.p. 185.5-186
at 750 mm.(118)	at 750 mm.(118)	at 750 mm.(118)	at 750 mm.(118)
$d_4^{20} = 0.8730$, $n_D^{20} = 1.4683$.	$d_4^{20} = 0.8730$, $n_D^{20} = 1.4683$.	$d_4^{20} = 0.8730$, $n_D^{20} = 1.4683$.	$d_4^{20} = 0.8730$, $n_D^{20} = 1.4683$.
mer Spiro[4.5]undecane	mer Spiro[4.5]undecane	mer Spiro[4.5]undecane	mer Spiro[4.5]undecane
(671e)	(671e)	(671e)	(671e)
mer, b.p. 185-186	mer, b.p. 185-186	mer, b.p. 185-186	mer, b.p. 185-186
at 748 mm.(118)	at 748 mm.(118)	at 748 mm.(118)	at 748 mm.(118)
$d_4^{20} = 0.8725$, $n_D^{20} = 1.4691$	$d_4^{20} = 0.8725$, $n_D^{20} = 1.4691$	$d_4^{20} = 0.8725$, $n_D^{20} = 1.4691$	$d_4^{20} = 0.8725$, $n_D^{20} = 1.4691$

Table 20. Isomerization of Bicyclanes and

Reactants		Catalyst (Per cent by weight on bicyclane + catalyst)	Contact Time (hours)	Temp. (°C.)
Bicyclane				
<i>cis</i> -Bicyclo[3.3.0]octane	AlCl ₃ (sublimed)	(28.6%)	2-48	room
<i>cis</i> -Bicyclo[4.3.0]nonane (<i>cis</i> -Hydrindane)	AlBr ₃ (anhydrous)	(43%)	12	100
Methylhydrindane	MoS ₃			high
<i>cis</i> -Bicyclo[4.4.0]decane (<i>cis</i> -Decalin)	Steel autoclave used		2	360-370
<i>cis</i> -Bicyclo[4.4.0]decane with some <i>trans</i> -Bicyclo[4.4.0]decane	Ni-Co-Al alloy		1	300
<i>cis</i> -Bicyclo[4.4.0]decane	Ni-Co-Al alloy		1.5	300
<i>cis</i> -Bicyclo[4.4.0]decane	MoS ₃ Steel autoclave used	(9.09%)	1.5	320-325
<i>cis</i> -Bicyclo[4.4.0]decane	MoS ₃ Steel autoclave used	(9.09%)	2	360-370
<i>cis</i> -Bicyclo[4.4.0]decane	MoS ₃ Steel autoclave used	(9.09%)	1	425-430
<i>cis</i> -Bicyclo[4.4.0]decane	AlBr ₃	(39.3%)	12	100
<i>cis</i> -Bicyclo[4.4.0]decane	AlBr ₃ HBr	(31.25%)		room
<i>cis</i> -Bicyclo[4.4.0]decane	AlCl ₃ (technical)	(28.6%)	22	room
<i>cis</i> -Bicyclo[4.4.0]decane	AlCl ₃	(24.3%)	12	100
<i>cis</i> -Bicyclo[4.4.0]decane	AlCl ₃ (technical)	(50%)	14	100
<i>cis</i> -Bicyclo[4.4.0]decane	AlCl ₃	(10%)	time of dis- tillation	175-210
<i>cis</i> -Bicyclo[4.4.0]decane (25.0%) <i>trans</i> -Bicyclo[4.4.0]decane (75.0%) ("Decalin")	AlCl ₃	(24.2%)	24	130
<i>trans</i> -Bicyclo[4.4.0]decane	MoS ₃			high
<i>cis</i> -9-Methyldecalin	AlCl ₃			20
1,10-Dimethyldecalin (mainly <i>cis</i>)	AlCl ₃	(50%)	2 days	room
3,6-Dimethyl-9-isopropylbicyclo- [5.3.0]decane (β -Vetivane)	AlCl ₃	(44.4%)	72	room

Bicyclanes with Saturated Side-Chains

Pressure (atms.)	Products (Per cent by weight on original bicyclane)		Refer- ences
	Isomers	Other Products	
1	Bicyclo[3.2.1]octane		(37)
1	<i>trans</i> -Bicyclo[4.3.0]nonane	AlBr ₃ +hydrocarbon complex	(674)
	Unidentified isomer	C ₂₇ H ₂₄ (m.p. 192–193°)	(293)
	Dimethylbicyclooctane		(449)
100–230	No isomers	<i>cis</i> -Bicyclo[4.4.0] decane	(545a)
(H ₂)			
50	<i>trans</i> -Bicyclo[4.4.0]decane		(545a)
(H ₂)			
50	<i>trans</i> -Bicyclo[4.4.0] decane	H ₂	(449)
(H ₂)		CH ₄	(449)
95–193	No isomers	<i>cis</i> -Bicyclo[4.4.0]decane	(449)
(H ₂)			
100–230	<i>trans</i> -Bicyclo[4.4.0]decane (52%)		(449)
(H ₂)			
100–245	<i>trans</i> -Bicyclo[4.4.0]decane (40%)	Decomposition products	(449)
(H ₂)	Dimethylbicyclo[3.3.0]octane		
	(8%)		(673)
1	<i>trans</i> -Bicyclo[4.4.0]decane (6%)		
	Isomer (b.p. 170–175°) (4%)		(674)
1	<i>trans</i> -Bicyclo[4.4.0]decane	C ₁₀ H ₁₈ (AlBr ₃) ₂	(676)
			(676)
1	<i>trans</i> -Bicyclo[4.4.0]decane (85%)	Lower-boiling products	(676)
1	<i>trans</i> -Bicyclo[4.4.0]decane	Lower-boiling products (50%)	(676)
1	<i>trans</i> -Bicyclo[4.4.0]decane		(677)
	(42.2%)		
1	<i>trans</i> -Bicyclo[4.4.0]decane	Alkanes	
	Dimethylbicyclo[3.3.0]octane	Cyclopentanes	
		Cyclohexanes	
1	<i>trans</i> -2,6-Dimethylbicyclo[3.3.0]-octane	Cyclohexane	(291)
		Methylcyclohexane	
		1,3,5-Trimethylcyclohexane	
		Decalins, mainly <i>trans</i> (50–70%)	(293)
	Dimethylbicyclooctane		(252)
1	<i>trans</i> -9-Methyldecalin		(351)
1	<i>trans</i> -1,10-Dimethyldecalin		(395b)
1	More-stable isomer (82.7%)		

Table 21. Isomerization of Bicy

Bicyclane	Reactants (Per cent by weight on bicyclane + catalyst)	Catalyst	Contact Time (hours)	Temp. (°C.)
<i>d</i> -Sabinene	Dilute (1 : 7) H ₂ SO ₄		4	b.p.
<i>d</i> -Sabinene	"Dilute H ₂ SO ₄ "			heated
<i>d</i> -Sabinene	H ₂ SO ₄ C ₂ H ₅ OH			heated
<i>d</i> -Sabinene	"50% H ₂ SO ₄ " CH ₃ . CO ₂ H	(6.5%) (46.7%)	0.25	room to 50
<i>d</i> -Sabinene	H . CO ₂ H	(50%)	0.25	-20
Camphene	"Suprax" glass			360-370
Camphene	"89% H ₃ PO ₄ "	(33.3%)	10	200
<i>dl</i> - α -Fenchene	H ₂ SO ₄	(trace)	7 min.	b.p.
<i>dl</i> - α -Fenchene	KHSO ₄	(36.3%)		
<i>dl</i> - α -Fenchene	KHSO ₄	(36.3%?)	15 min.	b.p.
<i>d</i> - β - Fenchene (Dd - Fenchene, probably with some γ -fenchene)	H ₂ SO ₄ (?)			
<i>d</i> - β - Fenchene (probably with some γ -fenchene)	H ₂ SO ₄ (small %)		several	heated
<i>d</i> - β - Fenchene (probably with some γ -fenchene)	C ₂ H ₅ OH (solvent)			
<i>d</i> - β - Fenchene (probably with some γ -fenchene)	2-Normal H ₂ SO ₄	(10.7%)	1.5	b.p.
<i>d</i> - β - Fenchene (probably with some γ -fenchene)	C ₂ H ₅ OH (solvent)	(53.1%)		
<i>d</i> - β - Fenchene (probably with some γ -fenchene)	H ₂ SO ₄	(trace)	2	b.p.
<i>d</i> - β - Fenchene (probably with some γ -fenchene)	KHSO ₄	(5.4%)		
<i>d</i> - β - Fenchene (probably with some γ -fenchene)	C ₂ H ₅ OH (solvent)	(56.3%)		
β -Pinene	"Suprax" glass			345-350
<i>d</i> - β -Pinene			175 g. β -pinene feed per hour	400-405
<i>l</i> - β -Pinene	Pd + H ₂		1	room
<i>l</i> - β -Pinene	Pd + H ₂		7	room
β -Pinene	Fuller's earth	(28.6%)	1.5	b.p.
β -Pinene	NiSO ₄ . H ₂ O	(2.44-2.91%)		140
β -Pinene	NiSO ₄ . H ₂ O	(1.96-2.91%)		140
β -Pinene	NiSO ₄ . H ₂ O			heated
β -Pinene	Acid-treated porcelain			150
β -Pinene	Acid-treated broken clay ware			heated
β -Pinene	Acid-treated permutite			
β -Pinene	Acid-treated bleaching earth			
β -Pinene	Acid-treated fuller's earth (used individually)			90
β -Pinene	Acid-treated permutite			
β -Pinene	Acid-treated silica gel (used individually)			
β -Pinene	HCl-treated ammonium tungstate			heated
β -Pinene	Steam-treated ammonium tungstate			
β -Pinene	HNO ₃ -treated ammonium tungstate			
β -Pinene	HCl-treated sodium tungstate			
β -Pinene	Steam-treated ammonium vanadate (used individually)			

clanes with Unsaturated Side-Chains

Pressure (atms.)	Products		Refer- ences
	Isomers (Per cent by weight on original bicyclane)	Other Products	
1	α -Terpinene		(622)
1	γ -Terpinene		(533)
1	<i>d</i> -1-Isopropyl-4-methylene-5-methylcyclopentene-1 "Terpinene"		(533)
1	<i>d</i> -1-Isopropyl-4-methylene-5-methylcyclopentene-1 "Terpinene"		(533)
1	<i>d</i> -1-Isopropyl-4-methylene-5-methylcyclopentene-1 "Terpinene"	4-Terpinenyl acetate (30%)	(533)
1	<i>d</i> -1-Isopropyl-4-methylene-5-methylcyclopentene-1 "Terpinene"	<i>d</i> -4-Terpinenyl formate	(533)
1	No isomers	Camphene unchanged	(12)
1	Bicyclic isomer	Diterpene	(201)
1	β -Fenchene		(320a)
1	γ -Fenchene		(320a)
1	β -Fenchene		(620a)
1	γ -Fenchene		(620a)
1	<i>l</i> - α -Fenchene		(320a)
1	<i>l</i> - α -Fenchene	Ethyl isofenchyl ether	(320a)
1	<i>l</i> -1-Methylsantene		(320a)
1	<i>l</i> - α -Fenchene (small %)	Ethyl isofenchyl ether	(320a)
1	<i>l</i> -1-Methylsantene (large %)		(12)
vapor phase with N ₂	Allo-ocimene (25%)	β -Pinene	(12)
	Dipentene		(217b)
	<i>l</i> -Limonene (13% on "Product")	β -Pinene (3% on "product")	
	Myrcene (about 67% on "Product")	Fraction, b.p. 48–62° at 20 mm. Hg, after removal of β -pinene (8.5% on "product")	
		Myrcene polymers (mainly α -camphorene) (9.5% on "product")	
1	<i>l</i> - α -Pinene		(466)
1	<i>l</i> - α -Pinene (96.1%)	"Dipinene"	(466)
1	"Terpinene"		(610)
1	Camphene		(503)
1	Camphene		(459a)
1	Camphene		(513)
1	Camphene		(509)
1	α -Pinene		(506)
1	α -Pinene		(506)
1	α -Pinene		(506)
1	Camphene		(505)
1	Camphene		(510)

Table 21. Isomerization of Bicy

Reactants		Catalyst (Per cent by weight on bicyclane + catalyst)	Contact Time (hours)	Temp. (°C.)
Bicyclane				
β -Pinene		HCl-treated ammonium tungstate Steam-treated ammonium tungstate HNO ₃ -treated ammonium tungstate HCl-treated sodium tungstate Steam-treated ammonium vanadate Steam-treated ammonium molybdate CH ₃ . CO ₂ H-treated sodium tungstate (used individually)		heated
β -Pinene (with some α -Pinene)		Borophosphoric acid (dried pieces) Cu tube used Steam (83.3% of pinenes + steam)		350
β -Pinene		Metaboric acid Titanic acids Simple and complex silicic acids Phosphorous and phosphoric acids Vanadic acids Antimonic acids Molybdic acids Phosphomolybdic acids Tungstic acids Phosphotungstic acids Chromoxalic acids (used individually)		heated
β -Pinene		Metavanadic acid (Total 4.76%)	25	100
β -Pinene		Metaboric acid Titanic acid Simple and complex silicic acids Vanadic acids Acid phosphates NaHSO ₄ Oxalic acid Phthalic acid Sulfonic acids (used individually)		heated
β -Pinene		Boric acid Titanic acid Silicic acid Vanadic acid Molybdic acid Antimonic acids Tungstic acids Borotungstic acids Silicotungstic acids Silicovanadic acids Borophosphoric acids Phosphostannic acid Phosphotungstic acid Phosphomolybdic acid Arsenomolybdic acid Boracetic acid Aluminoxalic acids Chromoxalic acids Acid phosphotungstates Magnesium acid phosphate Manganese acid phosphate Uranium acid phosphate (used individually)		heated
<i>l</i> - β -Pinene		H ₂ SO ₄ CH ₃ . CO ₂ H	1	60

Table 21. Isomerization of Bicyclanes

Reactants		Catalyst (Per cent by weight on bicyclane + catalyst)	Contact Time (hours)	Temp. (°C.)
Bicyclane				
β -Pinene		Organic acids Neutral solvents, such as toluene, xylene, or α - pinene (20–30%)		140–150
<i>l</i> - β -Pinene		Benzoic acid (47.6%)	30	125
<i>l</i> - β -Pinene		Benzoic acid (64.5%)	30	125
<i>l</i> - β -Pinene		Benzoic acid (73.0%)	30	125
<i>l</i> - β -Pinene		Benzoic acid (50%)	10–20	125–130
<i>l</i> - β -Pinene		Benzoic acid (30.5%)	30	123
		Toluene (solvent) (52.7%)		
<i>l</i> - β -Pinene		Benzoic acid		below 145
<i>l</i> - β -Pinene		Salicylic acid (67%)	12–20	160
<i>l</i> - β -Pinene		Abietic acid (81.8%)	10	130–135
<i>l</i> - β -Pinene		Abietic acid (81.8%)	20	130–135
<i>l</i> - β -Pinene		Abietic acid (81.8%)	10	145–150
<i>l</i> - β -Pinene		Abietic acid (81.8%)	20	145–150
<i>l</i> - β -Pinene		Abietic acid (81.8%)	10	160–165
<i>l</i> - β -Pinene		Abietic acid (81.8%)	20	160–165
<i>l</i> - β -Pinene		Abietic acid (81.8%)	10	175–180
<i>l</i> - β -Pinene		Abietic acid (81.8%)	20	175–180
<i>l</i> - β -Pinene		Colophony (75%)	15–20	“160–100”
<i>l</i> - β -Pinene		Trichlorophenol (74.4%)	30	145
<i>l</i> - β -Pinene		Picric acid (13.3%)	0.5	120
		Benzene (solvent) (20%)		
β -Pinene		Picric acid		b.p. (?)
<i>l</i> - β -Pinene		Stearin	30	145

with Unsaturated Side-Chains—Continued

Pressure (atms.)	Products (Per cent by weight on original bicyclane)		References (18)
	Isomers	Other Products	
	α -Pinene Other cyclic terpenes	Bornyl esters Isobornyl esters	
1	$\frac{l\text{-Limonene}}{l\text{-}\alpha\text{-Pinene}} = 0.1173$	Bornyl benzoate Isobornyl benzoate Fenchyl benzoate	(21)
1	$\frac{l\text{-Limonene}}{l\text{-}\alpha\text{-Pinene}} = 0.2484$	Bornyl benzoate	(21)
1	$\frac{l\text{-Limonene}}{l\text{-}\alpha\text{-Pinene}} = 0.5030$	Bornyl benzoate	(21)
1	α -Pinene (86%)	Bornyl benzoate (14%)	(20)
1	$l\text{-}\alpha\text{-Pinene}$	Bornyl benzoate	(21)
1	α -Pinene Limonene $l\text{-}\alpha\text{-Pinene}$ "Terpinene" } (50%)	Bornyl esters (35-36%)	(19) (19)
1	Camphene (?)		(19)
1	$l\text{-}\alpha\text{-Pinene}$ (1%)		(19)
1	Camphene (?)		(19)
1	$l\text{-}\alpha\text{-Pinene}$ (17%)		(19)
1	Camphene (?)		(19)
1	$l\text{-}\alpha\text{-Pinene}$ (23%)		(19)
1	Camphene (?)		(19)
1	$l\text{-}\alpha\text{-Pinene}$ (49.7%)		(19)
1	Camphene (?)		(19)
1	$l\text{-}\alpha\text{-Pinene}$ (52%)		(19)
1	Camphene (?)		(19)
1	$l\text{-}\alpha\text{-Pinene}$ (74.1%)		(19)
1	Camphene (?)		(19)
1	$l\text{-}\alpha\text{-Pinene}$ (75%)		(19)
1	Camphene (?)		(19)
1	$l\text{-}\alpha\text{-Pinene}$ (97.6%)		(20)
1	$l\text{-}\alpha\text{-Pinene}$ (70%)		(19)
1	$l\text{-}\alpha\text{-Pinene}$ (large %)	Bornyl esters (trace) Fenchyl esters (trace) d -Bornyl picrate (trace)	(19) (133)
	l -Camphene l -Limonene $l\text{-}\alpha\text{-Pinene}$	l -Bornyl picrate Isobornyl picrate d -Fenchyl picrate	
1	Camphene Dipentene	Bornyl picrate Diterpene	(322)
1	$l\text{-}\alpha\text{-Pinene}$ (70%)	H ₂ O (small amount)	(20)

Table 22. Isomeriza

Reactants		Catalyst (Per cent by weight on tricyclane + catalyst)	Contact Time (hours)	Temp. (°C.)
Tricyclane				
Cyclofenchene		Pt-charcoal		300
Cyclofenchene		Activated Florida earth	(short)	b.p.
Cyclofenchene		KHSO ₄	3	b.p.
		H ₂ SO ₄ , 1.35% in excess of theoretical		
Cyclofenchene		KHSO ₄	1	b.p.
		H ₂ SO ₄ , 1.36% in excess of theoretical		
Cyclofenchene		H ₃ PO ₄ , 85% H ₂ O, 15%	5	b.p.
Cyclofenchene		Phthalic anhydride	3.5	190–200
Tricyclene		Ni		180–200
Tricyclene		NaHSO ₄		168
Tricyclodecane, m.p. 77° (i.e., Tetrahydro-di-cyclopentadiene)		H ₂ SO ₄	(long)	above 77
		H ₂ S ₂ O ₇		
Tetradecahydroanthracene (liquid form)		Ni	4	270
Tetradecahydroanthracene (liquid form)		MoS ₃	1	at 330
			then	
			1	at 380
Tetradecahydroanthracene (liquid form)		AlCl ₃	0.25	100
Tetradecahydroanthracene (solid form)			1.50	460
Tetradecahydroanthracene (solid form)		MoS ₃	1.50	460
Tetradecahydroanthracene (solid form)		AlCl ₃	1.50	100
Tetradecahydroanthracene (solid form)		AlCl ₃	3	100
Tetradecahydrophenanthrene		MoS ₃	1	380
Tetradecahydrophenanthrene		AlCl ₃	1	100

tion of Tricyclanes

Pressure (atms.) (CO ₂)	Products (Per cent by weight on original tricyclane)		Refer- ences
	Isomers	Other Products	
	α -Fenchene β -Fenchene 1-Methylsantene		(669)
1	β -Fenchene γ -Fenchene	Polymers	(587)
1	(over 37.3%) (below 36.9%)		(320)
1	β -Fenchene} γ -Fenchene}	("100%")	(320)
1	1-Methylsantene	Cyclofenchene	(320)
bomb	β -Fenchene γ -Fenchene	<i>dl</i> -Isofenchyl alcohol <i>dl</i> -Isofenchyl acid phthalate	(320)
(N ₂)	<i>dl</i> -Camphene <i>dl</i> -Camphene		(369)
1	Tricyclodecane, m.p. 9°		(355)
high	Tetradecahydroanthracene	Tetradecahydroanthracene	(637)
(H ₂)	(solid form) (45%)	(liquid form) (55%)	(451)
98	Tetradecahydroanthracene		
(H ₂)	(solid form) (2.3%)		
1	Tetradecahydroanthracene		(451)
	(solid form) (25%)		
100	Tetradecahydrophenanthrene	Tetradecahydroanthracene	(451)
(H ₂)		(solid form) (22%)	
100	Tetradecahydrophenanthrene		(451)
(H ₂)			
1	Liquid form of tetradecahydro- anthracene (?)	Tetradecahydroanthracene	(451)
	Tetradecahydrophen- anthrene (?)	(solid form)	
	(68.9%)		
1	Liquid form of tetradecahydro- anthracene (?)		(451)
	Tetradecahydrophen- anthrene (?)		
	(67.5%)		
100	Tetradecahydroanthracene		(451)
(H ₂)	(solid form) (pure, 4.1%) (crude, 94%)		
1	Tetradecahydroanthracene		(451)
	(solid form) (19%) (25% with recycle of filtrate)		

Table 23. Isomerization of Cyclenes and

Cyclene	Reactants (Per cent by weight on cyclene + catalyst)	Catalyst	Contact Time (hours)	Temp. (°C.)
1-Methylcyclopropene-1	Al_2O_3			325
Cyclohexene	Al_2O_3 (commercial grade with some SiO_2)		5.5–6 g. feed per 121 cc. catalyst per hour (two passes)	450
Cyclohexene	BeO		5 g. feed per 44.2 cc. catalyst per hour (re - treated the b.p. 73.5–80.5° fraction from the initial product)	450
Cyclohexene	Silica gel		(one pass)	400
Cyclohexene	Silica gel		5.5–6 g. feed per hour (one pass)	450
Cyclohexene	TiO_2		5 g. feed per 88.4 cc. catalyst per hour (re - treated the b.p. 75–83° fraction from the initial product)	350
Cyclohexene	TiO_2		5 g. feed per 88.4 cc. catalyst per hour	400
Cyclohexene	TiO_2		5 g. feed per 88.4 cc. catalyst per hour	450
Cyclohexene	ThO_2 , V_2O_3 , ZrO_2 , or MnO			400–450
Cyclohexene	H_3PO_4 on silica		20 sec.	350
Cyclohexene	H_3PO_4 on silica		20 sec.	400
1-Methylcyclohexene-1	Quinoline-hydriodide			heated
4-Methylcyclohexene-1 (1-Methylcyclohexene-3)	Quinoline			
1-Methyl-4-isopropylcyclohexene-1 (Carvomenthene)	Silica gel			450
	Bleaching earth			300–450
	Pumice			
	Silica gel			
	"Tonsil"			
	Magnesium sulfate			
	Copper phosphate (used individually)			
1-Methyl-4-isopropylcyclohexene-1	Pumice			above 300
	Cu			
	Copper phosphate (used individually)			

Cyclenes with Saturated Side-Chains

Pressure (atms.)	Products			Refer- ences
	Isomers	(Per cent by weight on original cyclene) Other Products		
1	Butadiene-1,2 "Methylcyclopentene"		Cyclohexene	(373) (665)
1	"Methylcyclopentene"	(48.2%)	Cyclohexene	(12a)
1	"Methylcyclopentene"		Cyclohexene (?) Fraction, b.p. 200–205°	(665)
1	"Methylcyclopentene"	(44.8%)	Cyclohexene	(665)
1	"Methylcyclopentene"	(19%)	Cyclohexene	(12a)
1	"Methylcyclopentene"	(18%)	Cyclohexene	(12a)
1	"Methylcyclopentene"	(11%)	Cyclohexene Benzene	(12a)
1	No isomers		Benzene (small %)	(12a)
1 (vapor phase)	"Methylcyclopentene" (below 64%)		Hexane(s) (1.7%?) Cyclohexene (below 20%) Polymers (15%)	(529a)
1 (vapor phase)	"Methylcyclopentene" (below 65%)		Hexane(s) (1.7%?) Cyclohexene (below 17%) Polymers (17%)	(529a)
	Methylenecyclohexane	(2.5%)		(181)
1	"Dimethylcyclopentene"		1-Methylcyclohexene-3	(665)
	1-Isopropyl-4-methylcyclohexene-1 (Menthomenthene)	(50%)		(501)
	1-Isopropyl-4-methylcyclohexene-1			(507)

Table 23. Isomerization of Cyclenes and

Cyclene	Reactants (Per cent by weight on cyclene + catalyst)	Catalyst	Contact Time (hours)	Temp. (°C.)
1-Methyl-4-isopropylcyclohexene-1	Superficially-oxidized copper shavings (substantially CuO)			300-350
1-Methyl-4-isopropylcyclohexene-1	Pumice		(one recycle)	450
1-Methyl-4-isopropylcyclohexene-1	Pumice with 5% MgSO ₄			350
1-Methyl-4-isopropylcyclohexene-1	Granular copper phosphate with 0.5% H ₃ PO ₄			320-350
1-Methyl-4-isopropylcyclohexene-1	Pumice Bricks Silica gel (<i>i.e.</i> , activated silicic acid) Bleaching clay Fuller's earth Zeolites "Tonsil" (used individually or mixed with the following:) Copper oxide Copper sulfate Copper phosphate Magnesium oxide Magnesium phosphate Magnesium sulfate <i>p</i> -Toluenesulfonic acid C ₂ H ₅ OH			300-450
<i>d</i> -1-Methyl-4-isopropylcyclohexene-2 80% <i>d</i> -1-Methyl-4-isopropylcyclohexene-3 20% (This mixture had $\alpha_D = +100.79^\circ$)	<i>p</i> -Toluenesulfonic acid C ₂ H ₅ OH		(probably less than 4)	100
<i>d</i> -1-Methyl-4-isopropylcyclohexene-2 30% <i>d</i> -1-Methyl-4-isopropylcyclohexene-3 70% (This mixture had $\alpha_D = +91.0^\circ$)	<i>p</i> -Toluenesulfonic acid C ₂ H ₅ OH		2 4 8 (velocity study)	100
<i>d</i> -1-Methyl-4-isopropylcyclohexene-2 (below 30%) <i>d</i> -1-Methyl-4-isopropylcyclohexene-3 (above 70%) (This mixture had $\alpha_D = +93.3^\circ$)	<i>p</i> -Toluenesulfonic acid (21.8%) C ₂ H ₅ OH (34.5%)		18	100
<i>d</i> -1-Methyl-4-isopropylcyclohexene-3	<i>p</i> -Toluenesulfonic acid (20%) C ₂ H ₅ OH (40%)		24	b.p.
<i>d</i> -1-Methyl-4-isopropylcyclohexene-3	Silica gel		6 g. feed per 106 cc. catalyst per hour (two passes with intermediate fractional distillation)	375 or 400 or 450

Cyclenes with Saturated Side-Chains—Continued

Pressure (atms.)	Products			Refer- ences
	Isomers	(Per cent by weight on original cyclene) Other Products		
	1-Isopropyl-4-methylcyclohexene-1			(521)
	1-Isopropyl-4-methyl- cyclohexene-1	(87%)		(521)
	1-Isopropyl-4-methyl- cyclohexene-1	(60%)	Recycle stock	(521)
	1-Isopropyl-4-methyl- cyclohexene-1	(50-60%)	Recycle stock	(521)
	1-Isopropyl-4-methyl- cyclohexene-1	(50-90%)	Recycle stock	(521)
1	<i>dl</i> -1-Methyl-4-isopropyl- cyclohexene-3 Shown by optical rotation of product, $\alpha_D = +86.36^\circ$	(20%)	<i>d</i> -1-Methyl-4-isopropyl- cyclohexene-2 (80%)	(258a)
1	<i>dl</i> -1-Methyl-4-isopropyl- cyclohexene-3 Shown by optical rotations of product, $\alpha_D = +30.9^\circ$ after 2 hours $\alpha_D = +28.1^\circ$ after 4 hours $\alpha_D = +27.8^\circ$ after 8 hours	(70%)	<i>d</i> -1-Methyl-4-isopropyl- cyclohexene-2 (30%)	(258a)
1	<i>dl</i> -1-Methyl-4-isopropyl- cyclohexene-3 Shown by optical rotation of product, $\alpha_D = +28.3^\circ$	(above 70%)	<i>d</i> -1-Methyl-4-isopropyl- cyclohexene-2 (below 30%)	(258a)
1	<i>l</i> -1-Methyl-4-isopropyl- cyclohexene-3	(27.13%?)	<i>d</i> -1-Methyl-4-isopropyl- cyclohexene-3 (72.87%?)	(258)
1	Isomers claimed; product may contain: 1,1-Dimethyl-3-isopropylcyclo- pentenes, and/or 1,2-Dimethyl-3-isopropylcyclo- pentenes, and/or 1,3-Dimethyl-3-isopropylcyclo- pentenes, and/or 1-Ethyl-3-isopropylcyclopentenes, and/or 1-Methyl-3-isobutylcyclopentenes			(666)

Table 24. Isomerization of Cyclenes

Cyclene	Reactants		Contact Time (hours)	Temp. (°C.)
	Catalyst (Per cent by weight on cyclene + catalyst)			
1-Methyl-2-(3-butenyl)-cyclopentene-1(?)	P ₂ O ₅	(9.3%?)	5 (?)	140–150(?)
1-Vinylcyclohexene-3	H ₃ PO ₄ (sp. gr. 1.75)	(81.4%?)		200–235
<i>d</i> -1-Methyl-4-isopropenylcyclohexene-1 (<i>d</i> -Limonene)	"Floridin"		10	200
<i>d</i> -1-Methyl-4-isopropenylcyclohexene-1 (<i>d</i> -Limonene)			several	250–270
1-Methyl-4-isopropenylcyclohexene-1 (Limonene)			very long	250–270
<i>d</i> -1-Methyl-4-isopropenylcyclohexene-1 (<i>d</i> -Limonene)			5	275–290
<i>d</i> -1-Methyl-4-isopropenylcyclohexene-1 (<i>d</i> -Limonene)			6	380
1-Methyl-4-isopropenylcyclohexene-1 (Limonene)			several	380
<i>dl</i> -1-Methyl-4-isopropenylcyclohexene-1 (<i>dl</i> -Limonene; Dipentene)	Fuller's earth	(28.6%)	1.5	b.p.
1-Methyl-4-isopropenylcyclohexene-1 (Limonene)	"Floridin"			210–235
<i>dl</i> -1-Methyl-4-isopropenylcyclohexene-1 (<i>dl</i> -Limonene; Dipentene)	Activated clay (prepared from Chasov-Jarsky fire clay No. 5 by 6 hours treatment with 3 times its weight of 10% HCl, washing, and drying at 150–160°)	(0.51%)	1	170
<i>dl</i> -1-Methyl-4-isopropenylcyclohexene-1 (<i>dl</i> -Limonene; Dipentene)	Activated clay (prepared from Chasov-Jarsky fire clay No. 5 by 6 hours treatment with 3 times its weight of 10% HCl, washing, and drying at 150–160° C.)	(first hour) (0.5%) (second hour) (0.99%)	2 (removed the polymers after first hour)	170
1-Methyl-4-isopropenylcyclohexene-1 (Limonene)	H ₃ AsO ₄	(20.0%)	0.5	b.p.
<i>d</i> -1-Methyl-4-isopropenylcyclohexene-1 (<i>d</i> -Limonene)	H ₃ PO ₄		128	22–32
1-Methyl-4-isopropenylcyclohexene-1 (Limonene)	H ₃ PO ₄ on silica			150–250
<i>dl</i> -1-Methyl-4-isopropenylcyclohexene-1 (<i>dl</i> -Limonene; Dipentene)	H ₂ SO ₄ C ₂ H ₅ OH		1	100
1-Methyl-4-isopropenylcyclohexene-1 (Limonene)	Oxalic acid (anhydrous)		3 (?) at then 15 (?) at	90–100(?) 105–115(?)
<i>d</i> -1-Methyl-4-isopropenylcyclohexene-1 (<i>d</i> -Limonene)	C ₆ H ₅ · CO ₂ H		7	250
<i>d</i> -1-Methyl-4-isopropenylcyclohexene-1 (<i>d</i> -Limonene)	Acetone		6	300
<i>d</i> -1-Methyl-4-isopropenylcyclohexene-1 (<i>d</i> -Limonene)	Aniline		7	280
<i>d</i> -1-Methyl-4-isopropenylcyclohexene-1 (<i>d</i> -Limonene)	H ₂ O		10	290–360
1-Methyl-4-isopropylidenecyclohexene-1 (Terpinolene)	Acids			heated
1-(3-Butenyl)-cyclohexene-1	P ₂ O ₅	(30%)	3	140

with Unsaturated Side-Chains

Pressure (atms.)	Products				Refer- ences
	(Per cent by weight on original cyclene)		Other Products		
	Isomers				
	3a-Methyl-3a,4,7,7a-tetra- hydroindan (89%)		Unchanged hydrocarbon (11%)		(170)
	1-Ethylidenecyclohexene-2				(550)
	<i>dl</i> -Limonene (Dipentene) (trace)		<i>d</i> -Limonene (large %)		(107)
	<i>dl</i> -Limonene (Dipentene)		Polymer (trace)		(615)
	<i>dl</i> -Limonene (Dipentene)		Polymers		(108)
sealed tube	<i>dl</i> -Limonene (Dipentene) (small %)		<i>d</i> -Limonene (large %)		(107)
	<i>dl</i> -Limonene (Dipentene) (small %)		Polymer (5%)		(107)
	<i>dl</i> -Limonene (Dipentene) (small %)		<i>d</i> -Limonene (large %)		(107)
	<i>dl</i> -Limonene (Dipentene) (small %)		Polymer (5%)		(108)
1	"Terpinene"		"Dipinene"		(610)
	Isolimonene		Polymers		(550)
1	Terpinolene	(over 26.3% but less than 40.6%)	Dipentene	(over 46.5% but less than 60.8%)	(480a)
	Terpinolene		Polymers (12.9%)		
1	α -Terpinene (15.8%)		Dipentene (over 30%)		(480a)
	Terpinolene (over 14.83% but less than 23.46%)		<i>p</i> -Menthene-3 (5.76%)		
			<i>p</i> -Cymene (?) (25.02%)		
1	"Terpinene"				(208)
1	α -Terpinene (4%)		A diterpene (75%)		(209)
1	γ -Terpinene				(103)
1	Two bicyclic isomers		Tricyclic diterpene		(275a)
1	α -Terpinene		Resins		(617)
1	γ -Terpinene				
1	α -Terpinene				(394)
	<i>dl</i> -Limonene (trace?)		<i>d</i> -Limonene (large %)		(107)
	<i>dl</i> -Limonene (trace?)		<i>d</i> -Limonene (large %)		(107)
	<i>dl</i> -Limonene (trace?)		<i>d</i> -Limonene (large %)		(107)
	<i>dl</i> -Limonene (Dipentene) (small %)		<i>d</i> -Limonene (large %)		(107)
1	α -Terpinene		Polymer (10%)		(620)
1	γ -Terpinene				
1	1,2,3,4,5,6,7,8-Octahydro-naphthalene				(353)

Table 24. Isomerization of Cyclenes

Cyclene	Reactants (Per cent by weight on cyclene+catalyst)	Catalyst	Contact Time (hours)	Temp. (°C.)
1-Methyl-2-(3-butenyl)-cyclohexene-1	H ₃ PO ₄			130
Cycloisoprenemyrcene	H . CO ₂ H, 85% H ₂ O, 15%	(72.4%)	10 then 2	at 100 at 120
<i>l</i> -Zingiberene	"50% H ₂ SO ₄ " CH ₃ . CO ₂ H		6	60-65
α -Camphorene	H ₂ SO ₄ CH ₃ . CO ₂ H			
α -Camphorene	H . CO ₂ H, 95% H ₂ O, 5%		0.5	heated
α -Camphorene	H . CO ₂ H, 95% H ₂ O, 5%		3.5	heated
α -Carotene	Al ₂ O ₃ Solvent			room
α -Carotene	Activated Al ₂ O ₃ , 50% Inactive Al ₂ O ₃ , 50% Light petroleum+benzene (solvent)			room
α -Carotene	MgO Solvent			room
Neo- α -carotene	Al ₂ O ₃ Solvent			room
Pseudo- α -carotene	Solvent (?light petroleum+benzene)		2 months	-2
Pseudo- α -carotene	Solvent (?light petroleum+benzene)		24 hours 2 weeks 2 months (velocity study)	20 20 20
Pseudo- α -carotene	Light petroleum+benzene (solvent)		0.5	80
Pseudo- α -carotene	I ₂ (Benzine?)		0.5 1.0 (velocity study)	
Pseudo- α -carotene	Al ₂ O ₃ Solvent			room
β -Carotene	Light petroleum+benzene (equal volumes as solvent) (99.95%)		1 week 2 weeks 4 weeks 12 weeks (velocity study)	-2 -2 -2 -2
β -Carotene	Light petroleum+benzene (equal volumes as solvent) (used 5 ml. per 2.3 mg. β -carotene)		no delay	room
β -Carotene	Activated Al ₂ O ₃ , 33.3% Ordinary Al ₂ O ₃ , 66.7%	For simple chromatography		
β -Carotene	Light petroleum+benzene (solvent) In the dark		1 day 7 days 18 days 35 days 49 days (velocity study)	20 20 20 20 20
β -Carotene	Solvent (?light petroleum+benzene)		1 3 24 (velocity study)	40 40 40

with Unsaturated Side-Chains—Continued

Pressure (atms.)	Products (Per cent by weight on original cyclene)				Refer- ences
	Isomers	Other Products			
	<i>cis</i> -9-Methyl-1,4,5,6,7,8,9,10- octahydronaphthalene				(253)
1	Bicycloisoprenemyrcene (66.7%)				(484)
1					
1	<i>l</i> -Iso-zingiberene				(490)
					(495)
					(535)
	Bicyclic isomer				(537)
1	Bicyclic isomer				(494)
1	Tricyclic isomer				(494)
1	Neocarotene				(210)
1	Neocarotene	(30–33%)	α -Carotene		(211)
1	Neocarotene				(210)
1	β -Carotene		Neo- α -carotene		(211)
	Neocarotene				
1	β -Carotene	(5.5%)	Pseudo- α -carotene	(94.5%)	(102)
(N ₂)					
1	β -Carotene	(5%)	Pseudo- α -carotene	(95%)	(102)
1	β -Carotene	(20%)	Pseudo- α -carotene	(80%)	
1	β -Carotene	(47%)	Pseudo- α -carotene	(53%)	
1	β -Carotene	(68.7%)	Pseudo- α -carotene	(31.3%)	(102)
		(equilibrium value)			
1	β -Carotene	(49%)	Pseudo- α -carotene	(51%)	(661)
1	β -Carotene	(54%)	Pseudo- α -carotene	(46%)	
1	β -Carotene				(210)
1	Pseudo- α -carotene	(below 1.9%)	β -Carotene	(above 98.1%)	(102)
1	Pseudo- α -carotene	(1.7%)	β -Carotene	(98.3%)	
1	Pseudo- α -carotene	(below 3.0%)	β -Carotene	(above 97.0%)	
1	Pseudo- α -carotene	(2.5%)	β -Carotene	(97.5%)	
1	No isomers		β -Carotene unchanged		(102)
1					
1	Pseudo- α -carotene	(below 1%)	β -Carotene	(above 99%)	(102)
1	Pseudo- α -carotene	(5.5%)	β -Carotene	(94.5%)	
1	Pseudo- α -carotene	(6.2%)	β -Carotene	(93.8%)	
1	Pseudo- α -carotene	(10.0%)	β -Carotene	(90.0%)	
1	Pseudo- α -carotene	(11.1%)	β -Carotene	(88.9%)	
1					
1	Pseudo- α -carotene	(4%)	β -Carotene	(96%)	(102)
1	Pseudo- α -carotene	(5.4%)	β -Carotene	(94.6%)	
1	Pseudo- α -carotene	(11.2%)	β -Carotene	(88.8%)	

Table 24. Isomerization of Cyclenes

	Reactants	Catalyst	Contact Time	Temp.
	Cyclene	(Per cent by weight on cyclene + catalyst)	(hours)	(°C.)
β -Carotene		Solvent (?light petroleum + benzene)	1 3 (velocity study)	60 60
β -Carotene		Light petroleum (solvent) (used 75 ml. per 30 mg. β -carotene)	2 (evaporated to the point of crystallization)	70-80
β -Carotene		Light petroleum (solvent)	(evaporated to the point of crystallization)	b.p.
β -Carotene		Light petroleum + benzene (equal volumes as solvent)	1 3	77-80 77-80
β -Carotene		Activated Al_2O_3 , 33.3% } For simple chromatography Ordinary Al_2O_3 , 66.7% }	(velocity study)	
β -Carotene		Solvent (?light petroleum + benzene) $\text{Ca}(\text{OH})_2$ (For simple chromatography) (Benzine?)	(time to reach equilibrium composition)	80
β -Carotene		I_2 (0.1 mg. per 10 mg. β -carotene)	0.5-1.0	80
β -Carotene		Benzine	1.0	room (?)
β -Carotene		I_2 (Benzine?)	0.5 1.0 (velocity study)	room (?) room (?)
β -Carotene		Al_2O_3 Solvent		room
β -Carotene		Activated Al_2O_3 , 25% } Ordinary Al_2O_3 , 75% }	(several passes)	room
β -Carotene		Light petroleum (solvent) $\text{Ca}(\text{OH})_2$ Solvent		room
β -Carotene		$\text{KMnO}_4 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$ Benzene (solvent) Later, $\text{Ca}(\text{OH})_2$ adsorption Solvent	1.5 (oxidation)	room
Neocarotene				"crystallization"
1-Ethynylcyclohexene-1		20% Pt + 80% charcoal		200-205

with Unsaturated Side-Chains—Continued

Pressure (atms.)	Products (Per cent by weight on original cyclene)				Refer- ences
	Isomers		Other Products		
1	Pseudo- α -carotene	(7–8%)	β -Carotene	(92–93%)	(102)
1	Pseudo- α -carotene	(9.1–10.3%)	β -Carotene	(89.7–90.9%)	
1	Pseudo- α -carotene	(33.3%)	β -Carotene	(66.7%)	(102)
1	Pseudo- α -carotene	(27%)	β -Carotene	(73%)	(102)
1	Pseudo- α -carotene	(8–9%)	β -Carotene	(91–92%)	(102)
1	Pseudo- α -carotene	(31%)	β -Carotene	(69%)	
1	Pseudo- α -carotene	(29%)	β -Carotene	(71%)	(102)
1	Pseudo- α -carotene		β -Carotene		(661)
1	Pseudo- α -carotene		β -Carotene		(661)
1	Pseudo- α -carotene	(7%)	β -Carotene	(93%)	(661)
1	Pseudo- α -carotene	(12%)	β -Carotene	(88%)	
1	Pseudo- α -carotene				(210)
1	Pseudo- α -carotene	(40–50%)	Oxidation products	(50–60%)	(210)
1	Pseudo- α -carotene	(below 40%)			(210)
1	Pseudo- α -carotene		β -Apo-4-carotenal		(296)
			β -Carotenal		(297)
1	Neo- α -carotene				(211)
1 (CO ₂)	Ethylbenzene	(100%)			(344)

Table 25. Isomerization of Cyclo

Reactants		Catalyst (Per cent by weight on cyclodiene + catalyst)	Contact Time (hours)	Temp. (°C.)
Cyclodiene				
1-Methyl-4-isopropylcyclohexadiene-1,3 (α -Terpinene)	H_3PO_4		220	room
1-Methyl-4-isopropylcyclohexadiene-1,4 (γ -Terpinene)	Maleic anhydride (Reactant)	(Re- (42.1%)		heated
<i>l</i> -1-Methyl-4-isopropylcyclohexadiene-1,5 (<i>l</i> - α -Phellandrene)	H_3PO_4			room
<i>d</i> -1-Methyl-4-isopropylcyclohexadiene-1,5 (<i>d</i> - α -Phellandrene) [Elemi oil]	H_2SO_4 C_2H_5OH		few min.	room
1-Methyl-4-isopropylcyclohexadiene-1,5 (α -Phellandrene)	H_2SO_4 C_2H_5OH		several	b.p.

Table 26. Isomerization of Cyclo

Reactants		Catalyst (Per cent by weight on cyclodiene + catalyst)	Contact Time (hours)	Temp. (°C.)
Cyclodiene				
1,1-Dimethyl-4-methylenecyclohexadiene-2,5				160
1,1-Dimethyl-4-methylenecyclohexadiene-2,5	HCl (to saturation) $CH_3 \cdot CO_2H$ (solvent)		1	0
1,1,2-Trimethyl-4-methylene- cyclohexadiene-2,5	H_2SO_4 $CH_3 \cdot CO_2H$ (solvent)		1	0
1,1-Dimethyl-4-ethylidenecyclohexadiene-2,5	HCl (to saturation) $CH_3 \cdot CO_2H$ (solvent)	(68%)		20-40
1,1,3-Trimethyl-4-ethylidene- cyclohexadiene-2,5	70% H_2SO_4 $CH_3 \cdot CO_2H$ (solvent)	(34%) (45%)		
1,1-Dimethyl-4-propylidenecyclohexadiene-2,5	HCl $CH_3 \cdot CO_2H$ (solvent)			15-30
1,1,2,5-Tetramethyl-4-methylene- cyclohexadiene-2,5	HCl $CH_3 \cdot CO_2H$ (solvent)			b.p.
1,1,2,6-Tetramethyl-4-methylene- cyclohexadiene-2,5	H_2SO_4 $CH_3 \cdot CO_2H$ (solvent)		5	b.p.
<i>d</i> -1,2-Dimethyl-4-isopropenyl- cyclohexadiene-2,6	HCl, 2% $CH_3 \cdot CO_2H$, 98%	(83.3%)	5	b.p.
<i>d</i> -1-Methyl-2-ethyl-4-isopropenyl- cyclohexadiene-2,6	HCl, 2% $CH_3 \cdot CO_2H$, 98%	(84.0%)	5	b.p.
<i>d</i> -1-Methyl-2-propyl-4-isopropenylcyclohexadiene-2,6	HCl, 3% $CH_3 \cdot CO_2H$, 97%	(?%)	4	b.p. (?)
<i>l</i> - β -Curcumene	Inert gases used			380
<i>l</i> - β -Curcumene	Na $C_5H_{11}OH$			
<i>l</i> - β -Curcumene	H_2SO_4 , 10% H_2O , 90%		several	100

dienes with Saturated Side-Chains

Pressure (atms.)	Products (Per cent by weight on original cyclodiene)		References
	Isomers	Other Products	
1	No isomers	α -Terpinene recovered	(103)
1	α -Terpinene (isolated as maleic anhydride adduct) (corresponding yield of free α -terpinene is reported here)	(8.3%)	(206b)
1	α -Terpinene γ -Terpinene	(19.5%) A diterpene (40%)	(103)
1	α -Terpinene γ -Terpinene		(619)
1	α -Terpinene γ -Terpinene	Resins	(617)

dienes with Unsaturated Side-Chains.

Pressure (atms.)	Products (Per cent by weight on original cyclodiene)		References
	Isomers	Other Products	
1	1,2,4-Trimethylbenzene (?)	Condensation product	(22)
1	1,2,4-Trimethylbenzene		(23)
1	1,2,3,5-Tetramethylbenzene (small %)	Polymer (large %)	(23)
1	1,2-Dimethyl-4-ethylbenzene		(23)
1	1,2,5-Trimethyl-4-ethylbenzene		(23)
1	1,2-Dimethyl-4-propylbenzene		(23)
1	Pentamethylbenzene		(23)
1	Pentamethylbenzene		(23)
1	1,2-Dimethyl-4-isopropylbenzene (70.0%)		(311)
1	1-Methyl-2-ethyl-4-isopropylbenzene (63.2%)		(311)
1 (?)	1-Methyl-2-propyl-4-isopropylbenzene (60.0%)		(310)
(increased)	Isomer		(459)
	Isomer (b.p. 129-130° at 7 mm. Hg)		(459)
1	<i>l</i> -Bicyclic isomer (b.p. 115-117° at 7 mm. Hg)		(459)

Table 27. Isomerization of Bicyclenes and

Bicyclene	Reactants (Per cent by weight on bicyclene + catalyst)	Catalyst	Contact Time (hours) over 2 months 15 min.	Temp. (°C.) room b.p. heated
<i>d</i> - α -Thujene				
<i>d</i> - α -Thujene (partially racemized)	HCl (5%) in C ₂ H ₅ OH; used 100 cc. of this reagent per 41.7 g. or 50 cc. of the α -thujene			
α -Thujene	Maleic anhydride (Reactant)	(42.4%)		
α -Thujene	Benzoquinone (Reactant)	(23.8%)	2	b.p.
	0.05 <i>N</i> HCl (in C ₂ H ₅ OH)	(61.1%)		
<i>d</i> - α -Pinene			113.5	184.5
<i>d</i> - α -Pinene			115	184.6
<i>d</i> - α -Pinene	"Pyrex" reaction-vessel		12	200
<i>d</i> - α -Pinene	"Pyrex" reaction-vessel		50.5	200
<i>d</i> - α -Pinene	Carius tube used		50	200
<i>d</i> - α -Pinene	Carius tube used		100	200
<i>d</i> - α -Pinene	Carius tube used		200	200
<i>d</i> - α -Pinene			3.6	237
α -Pinene (American turpentine oil)			1	250-270
<i>d</i> - α -Pinene (American turpentine oil)			2	300
<i>l</i> - α -Pinene (French turpentine oil)			2	300
<i>d</i> - α -Pinene	"Pyrex" reaction-vessel		250-275 g. pinene per hour	370-375
<i>d</i> - α -Pinene	(Pumice?)		3.5	420
<i>d</i> - α -Pinene	Petroleum (solvent)		32.8	197.8
<i>d</i> - α -Pinene	Petroleum (solvent)		433 min.	217.9
<i>d</i> - α -Pinene	Acetophenone (solvent)		6	217.5
<i>d</i> - α -Pinene	1-Methylnaphthalene (solvent)		299 min.	218
α -Pinene	Activated Carbon			200

Bicyclenes with Saturated Side-Chains

Pressure (atms.)	Products (Per cent by weight on original bicyclene)		References
	Isomers	Other Products	
1	<i>l</i> - α -Thujene (small amount)	<i>d</i> - α -Thujene (principally)	(546)
1	α -Terpinene (isolated as maleic anhydride adduct) (18.7%) (corresponding yield of free α -terpinene is reported here)	α -Terpinene monohydrochloride α -Terpinene dihydrochloride	(206b)
1	γ -Terpinene (45%) <i>dl</i> - α -Phellandrene (isolated as maleic anhydride adduct) (3.1%) (corresponding yield of free α -phellandrene is reported here)	<i>p</i> -Cymene (41%)	(206b)
1	α -Terpinene (isolated as maleic anhydride adduct) (15.6%) (corresponding yield of free α -terpinene is reported here)		
1	α -Terpinene (isolated as benzoquinone adduct) (7.5%) (corresponding yield of free α -terpinene is reported here)	Quinhydrone	(206b)
vapor phase	Dipentene (<i>d</i> + <i>dl</i> - α -Pinene reported)	<i>d</i> - α -Pinene	(557)
liquid phase	Dipentene (<i>d</i> + <i>dl</i> - α -Pinene reported)	<i>d</i> - α -Pinene	(557)
vapor phase	Dipentene (10.5%)	<i>d</i> - α -Pinene	(112)
vapor phase	Dipentene (76.3%)	<i>d</i> - α -Pinene	(112)
liquid phase	Dipentene (90%)	<i>d</i> - α -Pinene	(112)
liquid phase	Dipentene (69%)	High-boiling residue (22%)	(112)
liquid phase	Dipentene (46%)	High-boiling residue (50%)	(112)
vapor phase	Dipentene (<i>d</i> + <i>dl</i> - α -Pinene reported)	<i>d</i> - α -Pinene	(557)
	Dipentene	Polymers	(615)
bomb	Dipentene	Polymer	(60)
bomb	Dipentene (20%)	<i>l</i> - α -Pinene	(462)
vapor phase with N ₂	Allo-ocimene (40% of product)	α -Pinene (3% of product)	(217a)
	Dipentene (42% of product)		
	α -Pyronene (6% of product)		
	β -Pyronene (6% of product)		
vapor phase with N ₂	Dipentene	α -Pinene (50%)	(105)
	Dipentene (<i>d</i> + <i>dl</i> - α -Pinene reported)	<i>d</i> - α -Pinene	(557)
	Dipentene (<i>d</i> + <i>dl</i> - α -Pinene reported)	<i>d</i> - α -Pinene	(557)
	Dipentene (<i>d</i> + <i>dl</i> - α -Pinene reported)	<i>d</i> - α -Pinene	(557)
	Dipentene (<i>d</i> + <i>dl</i> - α -Pinene reported)	<i>d</i> - α -Pinene	(557)
	Dipentene	Cymene C ₁₀ H ₁₈ (b.p. 164°)	(202)

Table 27. Isomerization of Bicyclenes and

Reactants		Catalyst	Contact Time	Temp.
Bicyclene	(Per cent by weight on bicyclene + catalyst)		(hours)	(°C.)
α -Pinene	Activated Carbon			300
α -Pinene	Steam			150–200
l - α -Pinene	Activated charcoal, Sillex, manganese oxide, or kieselguhr		1.5	145–150
	Activated charcoal (20%)			
l - α -Pinene	Activated charcoal			heated
l - α -Pinene	B_2O_3 or H_3BO_3			heated
	(Activated charcoal?)			
α -Pinene	Red phosphorus			100–200
l - α -Pinene	Al; $HgCl_2$; I_2		20	200–300
α -Pinene	Cu gauze			250
				300–350
dl - α -Pinene	Cu gauze			350
α -Pinene	Cu gauze		100 g. feed per hour	340
α -Pinene	Reduced Cu		70 g. feed per hour	340–350
α -Pinene	Reduced Cu (<i>via</i> $CuO + CH_3OH$)			340–350
α -Pinene	Reduced Cu; or glass			380–390
d - α -Pinene (French turpentine oil)	Fe			(?)
α -Pinene	Al_2O_3 (<i>via</i> ammonium alum + heat)		3.1 g. feed per 10 g. catalyst per minute	410
α -Pinene	Al_2O_3	(4.76%)	10	b.p.
α -Pinene (Turpentine oil)	Tikhvin bauxite	(40%)	4	50
α -Pinene (Turpentine oil)	Tikhvin bauxite	(40%)	4	70
α -Pinene (Turpentine oil)	Tikhvin bauxite	(40%)	4	100
α -Pinene (Turpentine oil)	Tikhvin bauxite	(40%)	8	100
α -Pinene (Turpentine oil)	Tikhvin bauxite	(40%)	2	115
α -Pinene (Turpentine oil)	Tikhvin bauxite	(40%)	4	115
α -Pinene (Turpentine oil)	Tikhvin bauxite	(40%)	8	115
α -Pinene (Turpentine oil)	Tikhvin bauxite	(40%)	4	125
α -Pinene (Turpentine oil)	Tikhvin bauxite	(40%)	2	150
α -Pinene (Turpentine oil)	Alapaevsk bauxite No. 1	(40%)	4	10
α -Pinene (Turpentine oil)	Alapaevsk bauxite No. 1	(40%)	4	20
α -Pinene (Turpentine oil)	Alapaevsk bauxite No. 1	(40%)	8	20
α -Pinene (Turpentine oil)	Alapaevsk bauxite No. 1	(40%)	2	45
α -Pinene (Turpentine oil)	Alapaevsk bauxite No. 2	(40%)	2	70

Table 27. Isomerization of Bicyclenes and

Reactants		Catalyst (Per cent by weight on bicyclene + catalyst)	Contact Time (hours)	Temp. (°C.)
Bicyclene				
α -Pinene (Turpentine oil)		Alapaevsk bauxite No. 2 (40%)	2	100
α -Pinene (Turpentine oil)		Alapaevsk bauxite No. 2 (40%)	2	100
α -Pinene (Turpentine oil)		Alapaevsk bauxite No. 2 (40%)	2	110
α -Pinene (Turpentine oil)		Alapaevsk bauxite No. 2 (40%)	4	110
α -Pinene (Turpentine oil)		Alapaevsk bauxite No. 2 (40%)	2	130
α -Pinene (Turpentine oil)		Alapaevsk bauxite No. 2 (40%)	2	150
α -Pinene		Al ₂ O ₃		100-200
		SiO ₂		200-300
		Kieselguhr		
		Kaolin		
		Clay		
		Fuller's earth		
		Aluminum phosphate		
		Calcium phosphate (used individually)		
<i>d</i> - α -Pinene (French turpentine oil)		CuO		240
α -Pinene		Copper chromite (Adkins')		300
α -Pinene		Copper chromite (Adkins')		400-410
α -Pinene		Copper chromite (Adkins')		375
α -Pinene		Co-Th catalyst (Fischer and Koch's)		340-400
<i>d</i> - α -Pinene		ThO ₂ , 25% Pumice, 75%	2.75	390
<i>d</i> - α -Pinene		ThO ₂ , 25% Pumice, 75%	3.5	420
α -Pinene		"Suprax" glass		340-350
α -Pinene		"Suprax" glass		345-350
α -Pinene		Ordinary soft-glass		350 (?)
α -Pinene		Fuller's earth (28.57%)	4	-20
				-5
				+25
				+158
<i>l</i> - α -Pinene		Fuller's earth (25%)		-20 to over room
<i>l</i> - α -Pinene		"Floridin"		room
α -Pinene (Turpentine oil)		Glukhov kaolin (20%)	2	50-60
α -Pinene (Turpentine oil)		Glukhov kaolin (20%)	2	60-70
α -Pinene (Turpentine oil)		Glukhov kaolin (20%)	4	60
α -Pinene (Turpentine oil)		Glukhov kaolin (20%)	2	70-80
α -Pinene (Turpentine oil)		Glukhov kaolin (20%)	2	90-100
α -Pinene (Turpentine oil)		Glukhov kaolin (20%)	0.25	100
α -Pinene (Turpentine oil)		Glukhov kaolin (20%)	2	25
α -Pinene (Turpentine oil)		Bobrik clay (20%)	2	50-60
α -Pinene (Turpentine oil)		Bobrik clay (20%)	2	50-60
α -Pinene (Turpentine oil)		Bobrik clay (20%)	4	50-60
α -Pinene (Turpentine oil)		Bobrik clay (20%)	2	80-90
α -Pinene (Turpentine oil)		Bobrik clay (20%)	0.20	100
α -Pinene (Turpentine oil)		Bobrik clay (20%)	25 min.	100
α -Pinene (Turpentine oil)		Cambrian clay (20%)	0.75	45
α -Pinene (Turpentine oil)		Cambrian clay (20%) (activated by 10% HCl for 6 hrs.)		
α -Pinene (Turpentine oil)		Cambrian clay (20%) (activated by 10% HCl for 6 hrs.)	0.50	60

[illegible]

Table 27. Isomerization of Bicyclenes and

Bicyclene	Reactants		Contact Time (hours)	Temp. (°C.)
	(Per cent by weight on bicyclene + catalyst)	Catalyst		
α -Pinene (Turpentine oil)	Cambrian clay (0.5%) (activated by 10% HCl for 6 hrs.)		0.50	b.p.
α -Pinene (Turpentine oil)	Latny clay "Extra" (20%)		20 min.	100
α -Pinene (Turpentine oil)	Latny clay (20%) (activated by 10% HCl for 6 hrs.)		0.75	45
α -Pinene (Turpentine oil)	Latny clay (20%) (activated by 10% HCl for 6 hrs.)		0.50	60
α -Pinene (Turpentine oil)	Latny clay (0.5%) (activated by 10% HCl for 6 hrs.)		0.50	b.p.
α -Pinene (Turpentine oil)	Chasov-Jarsky clay (20%)		2	80
α -Pinene (Turpentine oil)	Chasov-Jarsky clay (20%)		0.25	100
α -Pinene (Turpentine oil)	Chasov-Jarsky clay (20%)		2	100
α -Pinene (Turpentine oil)	Chasov-Jarsky clay (20%)		4	100
α -Pinene (Turpentine oil)	Chasov-Jarsky clay (20%)		2	120
α -Pinene (Turpentine oil)	Chasov-Jarsky clay (0.17%) Xylene (66.5%)		0.50	b.p.
α -Pinene (Turpentine oil)	Chasov-Jarsky clay (0.17%) Bromobenzene (66.5%)		0.50	160
α -Pinene (Turpentine oil)	Chasov-Jarsky clay (0.17%) Bromobenzene (66.5%)		1.50	160
α -Pinene (Turpentine oil)	Chasov-Jarsky clay (0.17%) Nitrobenzene (66.5%)		0.50	160
α -Pinene (Turpentine oil)	Chasov-Jarsky clay (0.17%) Nitrobenzene (66.5%)		1.50	160
α -Pinene (Turpentine oil)	Chasov-Jarsky clay (20%) (activated by 10% HCl for 6 hrs.)		0.75	45
α -Pinene (Turpentine oil)	Chasov-Jarsky clay (20%) (activated by 10% HCl for 6 hrs.)		0.50	60
α -Pinene (Turpentine oil)	Chasov-Jarsky clay (0.5%) (activated by 10% HCl for 6 hrs.)		0.50	b.p.
<i>d</i> - α -Pinene	Japanese acid clay (40%)		3	10
<i>d</i> - α -Pinene	Japanese acid clay (levi- gated by HCl, washed by H ₂ O, dried at 200- 250° C.) (11.9%) CH ₃ . CO ₂ H (26.0%) Acetic anhydride (2.6%) Activated clay (0.1 to 1%)		14	25
α -Pinene	MgSO ₄ . H ₂ O (4.76%)		10-30 min.	120
α -Pinene	ZnSO ₄ . H ₂ O FeSO ₄ . H ₂ O CoSO ₄ . H ₂ O NiSO ₄ . H ₂ O (used individually)			b.p.
α -Pinene	MgSO ₄ . H ₂ O on inactive carriers		50-60 drops feed for 94.25 cc. catalyst per min.	170

Bicyclenes with Saturated Side-Chains—*Continued*

Pressure (atms.)	Products (Per cent by weight on original bicyclene)				Refer- ences
	Isomers		Other Products		
1	Camphene	(60%)	Polymers	(9.5%)	(586)
1	Camphene	(56%)	Polymers	(16%)	(586)
1	Camphene	(50%)	Polymers	(16%)	(586)
1	Camphene	(52%)	Polymers	(16%)	(586)
1	Camphene	(62.5%)	Polymers	(10.5%)	(586)
1	Camphene	(below 20%)	Polymers	(8%)	(586)
1	Camphene	(53%)	Polymers	(16%)	(586)
1	Camphene	(50%)	Polymers	(12%)	(586)
1	Camphene	(44%)	Polymers	(21%)	(586)
1	Camphene	(44%)	Polymers	(20%)	(586)
1	Camphene	(40%)	Polymers	(15.0%)	(586)
1	Camphene	(35%)	Polymers	(2.5%)	(586)
1	Camphene	(50%)	Polymers	(10%)	(586)
1	Camphene	(41%)	Polymers	(1.6%)	(586)
1	Camphene	(50%)	Polymers	(6.0%)	(586)
1	Camphene	(52%)	Polymers	(15%)	(586)
1	Camphene	(58%)	Polymers	(12%)	(586)
1	Camphene	(56%)	Polymers	(16%)	(586)
1	<i>d</i> -Camphene } <i>d</i> -Limonene } Dipentene }	(64%)	Diterpenes	(16%)	(327)
1	<i>d</i> -Limonene		Bornyl acetate Isobornyl acetate <i>d</i> - α -Terpinyl acetate		(327a)
1	Camphene		Polymers		(349a)
1	Terpenes (b.p. 142.5–163°)				(459a)
1	Camphene				(503)
					(513)
1	Camphene				(503)
					(513)
vapor phase with N ₂	Camphene				(459a)
					(503)
					(513)

Table 27. Isomerization of Bicyclenes and

Bicyclene	Reactants (Per cent by weight on bicyclene + catalyst)	Catalyst	Contact Time (hours)	Temp. (°C.)
α -Pinene (Turpentine oil)	$\text{NiSO}_4 \cdot \text{H}_2\text{O}$			120–130
α -Pinene	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$ $\text{NiSO}_4 \cdot \text{H}_2\text{O}$ (used individually)			heated
α -Pinene	CaHPO_4	(total 4.76%)	(long)	140
α -Pinene (Turpentine oil)	Sec. manganese phosphate	(1.19%)	(long)	b.p.
α -Pinene	Acid-treated Permutite Acid-treated silica gel (used individually)			90
α -Pinene	HCl-treated ammonium tungstate Steam-treated ammonium tungstate HNO_3 -treated ammonium tungstate HCl-treated sodium tungstate Steam-treated ammonium vanadate (used individually)			heated
α -Pinene	HCl-treated ammonium tungstate Steam-treated ammonium tungstate HNO_3 -treated ammonium tungstate HCl-treated sodium tungstate Steam-treated ammonium vanadate Steam-treated ammonium molybdate $\text{CH}_3 \cdot \text{CO}_2\text{H}$ -treated sodium tungstate (used individually)			heated
α -Pinene	Meta-boric acid Titanic acids Simple and complex silicic acids Phosphorous and phosphoric acids Vanadic acids Antimonic acids Molybdic acids Phosphomolybdic acids Tungstic acids Phosphotungstic acids Chromoxalic acids (used individually)			heated
α -Pinene	Phosphomolybdic acid	(total 3.84%)	200	20–30
α -Pinene	Phosphomolybdic acid	(total 3.84%)	200	20–30
α -Pinene	Meta-boric acid Titanic acid Simple and complex silicic acids Vanadic acids Acid phosphates NaHSO_4 Oxalic acid Phthalic acid Sulfonic acids (used individually)			heated
α -Pinene	Tungstic acid (total 4.76–5.66%)		49.5–59.5	120
α -Pinene	Tungstic acid (total 5.66%)		30–40	130
α -Pinene	Titanic acid (freshly prepared)	(0.1%)	20–30	b.p.
α -Pinene	Titanic acid	(0.1%)	20–30	b.p.
α -Pinene	Metavanadic acid (total 4.76%)		25	100
α -Pinene	Borophosphoric acid	(total 5.66–7.4%)	300–400	120

1 Hydrocarbon with Continued

1 Hydrocarbon with Continued

1 Hydrocarbon with Continued

1 Hydrocarbon with Continued

Products

Products

Products

Products

by weight on original

by weight on original

by weight on original

by weight on original

Camphene

Camphene

Camphene

Camphene

Camphene

Camphene

Camphene

Camphene

Camphene

Camphene

Camphene

Camphene

Camphene

Camphene

Camphene

Camphene

Camphene

Camphene

Camphene

Camphene

Camphene

Camphene

Camphene

Camphene

Camphene

Camphene

Camphene

Camphene

Table 27. Isomerization of Bicyclenes and

Bicyclene	Reactants	Catalyst	Contact Time	Temp.
	(Per cent by weight on bicyclene + catalyst)		(hours)	(°C.)
α -Pinene	Borophosphoric acid and pumice (compressed into pieces) Cu tube used Steam (80% on α -pinene plus steam)			325
α -Pinene	Boracetic acid	(4.76%)	(long)	100–145
α -Pinene	Boric acid		(long)	heated
	Titanic acid			
	Silicic acid			
	Vanadic acid			
	Molybdic acid			
	Antimonic acids			
	Tungstic acids			
	Borotungstic acids			
	Silicotungstic acids			
	Silicovanadic acids			
	Borophosphoric acids			
	Phosphostannic acid			
	Phosphotungstic acid			
	Phosphomolybdic acid			
	Arsenomolybdic acid			
	Boroacetic acid			
	Aluminoxalic acids			
	Chromoxalic acids			
	Acid phosphotungstates			
	Magnesium acid phosphate			
	Manganese acid phosphate			
	Uranium acid phosphate (used individually)			
<i>l</i> - α -Pinene	H_3AsO_4	(2.44%)	3	b.p.
<i>l</i> - α -Pinene	H_3AsO_4	(1.23%)	3	b.p.
<i>l</i> - α -Pinene	H_3AsO_4	(20.0%)	0.5	b.p.
α -Pinene	Antimonic acid (dried 40 min. at 168–170°)	(total 5–10%)	250–500	50–70
α -Pinene	Antimonic acid (total 7.4–13.8%)		133–266	60–100
α -Pinene	Antimonic acid (total 4.76%)		83	120
α -Pinene	Antimonic acid (total 4.76%)		83	120
α -Pinene	0.442 <i>N</i> HCl C_2H_5OH			
α -Pinene	1.379 <i>N</i> HCl C_2H_5OH			
α -Pinene (American turpentine oil)	25% HCl (16.67% by volume) C_2H_5OH (16.67% by volume)		several	100
α -Pinene (American turpentine oil)	HNO_3 (sp. gr. 1.255) (16.67%) C_2H_5OH (16.67%)			warmed
α -Pinene	1 Normal H_3PO_4			
α -Pinene	3.5 Normal H_3PO_4 C_2H_5OH		5	

Bicyclenes with Saturated Side-Chains—*Continued*

Pressure (atms.)		Products		Refer- ences
		Isomers	Other Products	
1	Camphene	(70–80%)		(511)
1	Camphene		Bornyl acetate (2%)	(514)
1	Camphene	(to 85%)		(514)
1	Terpinene		<i>l</i> - α -Pinene (large %)	(208)
			Cymene	
			Terpineol	
			H ₃ AsO ₄ (60% recovered)	(209)
			As ₂ O ₃ (0.5%)	
1	Terpinene		α -Pinene	(208)
			Cymene (small %)	
			Terpineol (small %)	
1	Terpinene	(over 60%)	Cymene (below 20%)	(208)
			Terpineol (1%)	(209)
1	Camphene	(large %)	Terpene alcohols (small %)	(512)
1	Camphene		Terpene alcohols (small %)	(514)
1	Camphene	(large %)	Terpene alcohols (small %)	(502)
1	Camphene		"Other hydrocarbons" (small %)	(601a)
			Terpene alcohols	
	Camphene		Bornyl chloride	(256)
	Dipentene		Terpineol	
			C ₁₀ H ₁₇ OC ₂ H ₅	
			Terpin hydrate	
	Dipentene		Bornyl chloride	(256)
			Dipentene hydrochloride	
1	Dipentene	(small %)	Chlorinated products (large %)	(615)
1	Dipentene			(615)
	No isomers			(255)
	Camphene		Terpineol	(255)
	Dipentene		C ₁₀ H ₁₇ OC ₂ H ₅	
			C ₁₀ H ₁₆ . H ₃ PO ₄	

Table 27. Isomerization of Bicyclenes and

Bicyclene	Reactants		Catalyst (Per cent by weight on bicyclene + catalyst)	Contact Time (hours)	Temp. (°C.)
α -Pinene	10 Normal H_3PO_4				
α -Pinene	"70% H_3PO_4 "		(13.98%)	5	75
d - α -Pinene	H_3PO_4			100	room
l - α -Pinene	H_3PO_4 (sp. gr. 1.7)		(4.76%?)		60-70
	$\text{CH}_3 \cdot \text{CO}_2\text{H}$		(63.5%?)		
l - α -Pinene	H_3PO_4 (sp. gr. 1.7)		(2.1%)	0.5	b.p
	$\text{CH}_3 \cdot \text{CO}_2\text{H}$		(31%)		
	Pumice powder		(1.7%)		
α -Pinene (Turpentine oil)	"50% H_2SO_4 "		(32%)	24	50
α -Pinene (American- d - or French- l -turpentine oil)	Dilute H_2SO_4 (1 : 1 by vol. of H_2O and H_2SO_4)				80
d - α -Pinene	H_2SO_4		(33.3%)	6.333	-2
	H_2O		(20.4%)		
d - α -Pinene	H_2SO_4		(35.0%)	6.5	-3
	H_2O		(16.4%)		
d - α -Pinene	H_2SO_4		(35.0%)	5	-8
	H_2O		(16.4%)		
d - α -Pinene	H_2SO_4		(23.6%)	7.5	-3
	H_2O		(11.1%)		
l - α -Pinene (French turpentine oil)	H_2SO_4		(4.76%)	24	room
α -Pinene	H_2SO_4				
α -Pinene (American turpentine oil)	H_2SO_4		(7.0%)	2-3 days	
α -Pinene (d -American or l -French turpentine oil)	H_2SO_4		(9.7%)		70-130
α -Pinene	0.03N H_2SO_4				
	$\text{C}_2\text{H}_5\text{OH}$				
α -Pinene	1.5928N H_2SO_4				
	$\text{C}_2\text{H}_5\text{OH}$				
d - α -Pinene	H_2SO_4		(18.8%)	5	-3
	$\text{C}_2\text{H}_5\text{OH}$		(17.6%)		
	HgSO_4		(3.8%)		
	H_2O		(7.7%)		
d - α -Pinene	H_2SO_4		(19.5%)	5	-3
	$\text{C}_2\text{H}_5\text{OH}$		(18.3%)		

Bicyclenes with Saturated Side-Chains—*Continued*

Pressure (atms.)	Products (Per cent by weight on original bicyclene)		Refer- ences
	Isomers	Other Products	
	Terpinolene	Cineol	(255)
		Cymene	
1	$\frac{\text{Dipentene}}{\text{Terpinolene}} = 7.08$	Polymerization products	(542)
	α -Terpinene (11%)	A diterpene (75%)	(103)
1	<i>l</i> -Limonene		(448)
1	<i>l</i> -Limonene (56.3%)		(448)
1	Camphene	Cineol (0.66%)	(149)
	Dipentene	Cymene	
	Limonene	Four new substances	
	α -Terpinene	Polymers (67%)	
	γ -Terpinene		
1	Terpinolene		
	"Terpilene," which is di- pentene + "terpinene" + terpinolene	Cymene $\text{C}_{10}\text{H}_{20}$ Colophony (small %)	(14)
1	Dipentene	Borneol	(105)
	Terpinolene (2.1%)	α -Pinene (3.8%) Terpineol (3.8%) Terpin hydrate (73.9%) Polymer (6.5%)	
1	Dipentene	Borneol	(105)
	Terpinolene (2.9%)	Terpineol (5.1%) Terpin hydrate (72.4%) Polymer (6.6%)	
1	Dipentene	Borneol	(105)
	Terpinolene (4.4%)	α -Pinene (22.0%) Terpineol (4.4%) Terpin hydrate (44.0%) Polymer (4.6%)	
1	Dipentene	Borneol	(105)
	Terpinolene (6.0%)	Terpineol (7.9%) Terpin hydrate (42.5%) Polymer (14.7%)	
1	<i>dl</i> -Camphene (10%)	Cymene (6-8%)	(462)
	Terpinolene	Colophony	(464)
			(616)
			(617)
	α -Terpinene		(617)
1	γ -Terpinene		
	<i>dl</i> -Camphene (20%)	Cymene	(13)
	"Terpilene," which is Di- pentene + "Terpinene" + Terpinolene	$\text{C}_{10}\text{H}_{20}$ Polymers	(14)
	Dipentene	$\text{C}_{10}\text{H}_{17}\text{OC}_2\text{H}_5$	(254)
	Terpinolene		
	α -Terpinene	Cymene	(254)
	Terpinolene	Cineol	
		Terpin hydrate	
		α -Terpineol	
		$\text{C}_{10}\text{H}_{17}\text{OC}_2\text{H}_5$	
1	Dipentene	α -Pinene (18.4%)	(105)
	Terpinolene (3.8%)	Terpineol (32.6%) Terpin hydrate (1.2%) Polymer (2.2%)	
1	Dipentene	α -Pinene (14.7%)	(105)
	Terpinolene (7.5%)	Terpineol (28.2%)	

Table 27. Isomerization of Bicyclenes and

Bicyclene	Reactants		Catalyst (Per cent by weight on bicyclene + catalyst)	Contact Time (hours)	Temp. (°C.)
<i>d</i> - α -Pinene (<i>Continued</i>)	H_2O		(8.0%)		
<i>d</i> - α -Pinene	H_2SO_4	(19.5%)	12	0	
	$\text{C}_2\text{H}_5\text{OH}$	(18.3%)			
	H_2O	(8.0%)			
<i>l</i> - α -Pinene (French turpentine oil)	H_2SO_4 (sp. gr. 1.64)	(16.67%)		100	
	$\text{C}_2\text{H}_5\text{OH}$	(16.67%)			
α -Pinene (American turpentine oil)	H_2SO_4 (sp. gr. 1.64)	(16.67%)	24	100	
	$\text{C}_2\text{H}_5\text{OH}$	(16.67%)			
α -Pinene + β -Pinene (Russian turpentine oil)	H_2SO_4 (sp. gr. 1.64)	(16.67%)	several days	100	
	$\text{C}_2\text{H}_5\text{OH}$	(16.67%)			
<i>d</i> - α -Pinene	H_2SO_4	(20.3%)	5.5	-5	
	$\text{C}_2\text{H}_5\text{OH}$	(19.1%)			
	H_2O	(4.1%)			
<i>d</i> - α -Pinene	H_2SO_4	(17.7%)	6	-4	
	$\text{C}_2\text{H}_5\text{OH}$	(33.2%)			
<i>d</i> - α -Pinene	H_2SO_4	(21.2%)	1.5	at	0
	$\text{C}_2\text{H}_5\text{OH}$	(19.9%)	then 0.5	at	20
			then 1.0	at	65-70
<i>d</i> - α -Pinene	H_2SO_4	(21.2%)	3		-10
	$\text{C}_2\text{H}_5\text{OH}$	(19.9%)			
<i>d</i> - α -Pinene	H_2SO_4	(21.2%)	9.25		-8
	$\text{C}_2\text{H}_5\text{OH}$	(19.9%)			
<i>d</i> - α -Pinene	H_2SO_4	(21.2%)	4		0
	$\text{C}_2\text{H}_5\text{OH}$	(19.9%)			
<i>d</i> - α -Pinene	$\text{H} \cdot \text{CO}_2\text{H}$	(25.3%)	2 months plus 6 days	room	
<i>l</i> - α -Pinene (French turpentine oil)	$\text{H} \cdot \text{CO}_2\text{H}$	(33.7%)	26 days	room	
<i>d</i> - α -Pinene (American turpentine oil)	$\text{H} \cdot \text{CO}_2\text{H}$	(33.3%)	67 days	room	
<i>l</i> - α -Pinene	$\text{H} \cdot \text{CO}_2\text{H}$	(37.4%)	2 years (?)	room	
	H_2O	(7.3%)			
<i>l</i> - α -Pinene	$\text{H} \cdot \text{CO}_2\text{H}$	(23.0%)	2 years (?)	room	
	H_2O	(9.0%)			
<i>l</i> - α -Pinene	$\text{H} \cdot \text{CO}_2\text{H}$	(19.5%)	2 years (?)	room	
	H_2O	(22.9%)			
<i>l</i> - α -Pinene	$\text{H} \cdot \text{CO}_2\text{H}$	(16.8%)	2 years (?)	room	
	H_2O	(33.2%)			

Bicyclenes with Saturated Side-Chains—Continued

Pressure (atms.)	Products			Refer- ences
	Isomers	(Per cent by weight on original bicyclene)	Other Products	
1	Dipentene Terpinolene	(9.9%)	Terpin hydrate (1.6%) Polymer (1.8%) Terpineol (29.9%) Terpin hydrate (7.1%) Polymer (5.1%)	(105)
1	Dipentene			(191)
1	α -Terpinene		Cymene	(615)
1	γ -Terpinene			(616)
1	γ -Terpinene			(669a)
1	Terpinolene			
1	Dipentene			
1	Terpinolene	(21.1%)	α -Pinene (12.9%) Terpineol (18.2%) Terpin hydrate (1.5%) Polymer (2.1%)	(105)
1	Terpinolene	(6.8%)	α -Pinene (49.3%) Terpineol (2.2%) Polymer (11.8%)	(105)
1	Terpinolene	(17.6%)	Polymer (54.8%)	(105)
1	Terpinolene	(22.0%)	α -Pinene (17.6%) Terpineol (5.9%) Polymer (4.8%)	(105)
1	Terpinolene	(24.5%)	α -Pinene (9.2%) Terpineol (6.3%) Terpin hydrate (1.5%) Polymer (9.6%)	(105)
1	Terpinolene	(25.2%)	Terpineol (2.94%) Polymer (7.35%)	(105)
1	<i>d</i> -Camphene <i>d</i> -Limonene Dipentene α -Terpinene Terpinolene	(14.7%) (1.84%)	H ₂ CO ₂ H (recovered 41.3%) <i>d</i> - α -Pinene (below 17%) <i>d</i> -Diterpilene (10%) Bornyl formate (8.1%) <i>d</i> -1-Terpinenyl formate (51.5%) <i>d</i> -1-Terpinenyl formate (51.5%) <i>d</i> - α -Terpinyl formate (51.5%)	(460)
1	<i>l</i> -Limonene		<i>l</i> - α -Pinene (13.4%) Cymene <i>l</i> -Diterpilene α -Terpinyl formate (large %) Bornyl formate (?)	(328)
1	<i>d</i> -Limonene		<i>d</i> - α -Pinene Cymene <i>l</i> -Diterpilene <i>d</i> - α -Terpinyl formate	(328)
sealed tube	Dipentene	(small %)	Diterpilene (large %) <i>l</i> -Bornyl formate (trace)	(78)
sealed tube	<i>l</i> -Limonene		Terpin hydrate (large %) α -Terpinyl formate	(78)
sealed tube	<i>l</i> -Limonene		<i>l</i> - α -Pinene Terpin hydrate (3.7%) <i>l</i> - α -Terpinyl formate	(78)
sealed tube	<i>l</i> -Limonene		<i>l</i> - α -Pinene Terpin hydrate (2.6%) <i>l</i> - α -Terpinyl formate (7.3%)	(78)

Table 27. Isomerization of Bicyclenes and

Reactants		Catalyst	Contact Time	Temp.
Bicyclene	(Per cent by weight on bicyclene + catalyst)		(hours)	(°C.)
<i>l</i> - α -Pinene (French turpentine oil)	$\text{CH}_3 \cdot \text{CO}_2\text{H}$	(71%)	0.5 year	room
<i>d</i> - α -Pinene (American turpentine oil)	$\text{CH}_3 \cdot \text{CO}_2\text{H}$			100
<i>l</i> - α -Pinene (French turpentine oil)	$\text{CH}_3 \cdot \text{CO}_2\text{H}$	(67.0%)	64 then 2 months	at room
<i>l</i> - α -Pinene (French turpentine oil)	$\text{CH}_3 \cdot \text{CO}_2\text{H}$	(30.6%)	5	200
<i>l</i> - α -Pinene	$\text{CH}_3 \cdot \text{CO}_2\text{H}$ ZnCl_2	(62.0%) (6.9%)	"overnight"	room
<i>l</i> - α -Pinene	$\text{CH}_3 \cdot \text{CO}_2\text{H}$ H_2O	(45.2%) (3.4%)	3 years	room
<i>l</i> - α -Pinene	$\text{CH}_3 \cdot \text{CO}_2\text{H}$ H_2O	(28.0%) (8.4%)	3 years	room
<i>l</i> - α -Pinene	$\text{CH}_3 \cdot \text{CO}_2\text{H}$ H_2O	(25.8%) (15.5%)	3 years	room
<i>l</i> - α -Pinene (French turpentine oil)	$\text{CH}_3 \cdot \text{CO}_2\text{H}$ (below 50%) 50% Soln. of $\text{C}_6\text{H}_5 \cdot \text{SO}_3\text{H}$ Acetic anhydride to remove H_2O		1.5-2	76
<i>d</i> - α -Pinene	$\text{ClCH}_2 \cdot \text{CO}_2\text{H}$	(20.0%)	35	140-142
<i>d</i> - α -Pinene	$\text{ClCH}_2 \cdot \text{CO}_2\text{H}$ (1 mole per 3 moles α -pinene) Boracetic anhydride		25	100
<i>d</i> - α -Pinene	$\text{CH}_3 \cdot \text{CO}_2\text{H}$ (solvent) $\text{Cl}_2\text{CH} \cdot \text{CO}_2\text{H}$	(33.3%)	0.5	90
<i>d</i> - α -Pinene	Oxalic acid (anhydrous) Tetrachloroethane (sol-vent)	(7.14%) (35.7%)	4	140
<i>l</i> - α -Pinene (?) + <i>l</i> - β -Pinene (?) (Turpentine oil, b.p. 158-161°)	Oxalic acid (anhydrous)	(20%)	3 then 15	at 90-100 at 105-115
α -Pinene	$\text{C}_6\text{H}_5 \cdot \text{CO}_2\text{H}$	(50%)	10-20	125-130

Bicyclenes with Saturated Side-Chains—Continued

Pressure (atms.)	Isomers	Products (Per cent by weight on original bicyclene)		Refer- ences (74)
		Isomers	Other Products	
sealed tube	<i>l</i> -Limonene		<i>l</i> - α -Pinene <i>l</i> -Bornyl acetate (<i>Ld</i>)-Fenchyl acetate <i>l</i> - α -Terpinyl acetate	(74)
1	<i>d</i> -Limonene		<i>d</i> - α -Pinene <i>d</i> -Bornyl acetate <i>l</i> -Bornyl acetate <i>d</i> - α -Terpinyl acetate	(328)
1	<i>l</i> -Camphene <i>l</i> -Limonene		<i>l</i> - α -Pinene <i>l</i> -Bornyl acetate (<i>Ld</i>)-Fenchyl acetate α -Terpinyl acetate	(75)
autoclave	"Camphene" <i>l</i> -Limonene (or else di- pentene)	(10–15%) (30–40%)	"Bornyl acetate" (30–40%)	(662)
1	<i>l</i> -Limonene		α -Pinene <i>l</i> - α -Terpinyl acetate $C_{10}H_{17}Cl$ (m.p. 47–109°)	(171)
sealed tube (CO ₂)	<i>l</i> -Limonene		α -Pinene Terpin hydrate (0.07%) α -Terpinyl acetate	(78)
sealed tube (CO ₂)	<i>l</i> -Limonene		α -Pinene Terpin hydrate (trace) α -Terpinyl acetate	(78)
sealed tube (CO ₂) 1	<i>l</i> -Limonene Camphene		α -Pinene α -Terpinyl acetate <i>l</i> - α -Pinene Bornyl acetate Isobornyl acetate (<i>Ld</i>)-Fenchyl acetate <i>l</i> - α -Terpinyl acetate $C_{10}H_{18}$ (b.p. 157–160°)	(78) (35) (36)
1	Camphene <i>d</i> - δ -Fenchene (?) <i>d</i> -Limonene + dipentene Terpinolene	(11.4%) (3.35%) (42.2%) (8.71%)	<i>d</i> - α -Pinene (1.34%) <i>d</i> -Borneol Isoborneol <i>l</i> -Fenchyl alcohol <i>d</i> -Bornyl chloracetate Isobornyl chloracetate <i>l</i> -Fenchyl chloracetate } (53%) $ClCH_2 \cdot CO_2H$ (16% unreacted) H_2O (trace)	(133a)
1	<i>d</i> + <i>dl</i> -Camphenes <i>d</i> -Limonene + dipentene Terpinolene		Bornyl chloracetate Isobornyl chloracetate Fenchyl chloracetate } (51%)	(133a)
1	<i>d</i> -Limonene α -Terpinene		<i>d</i> - α -Pinene <i>d</i> -Bornyl dichloracetate Isobornyl dichloracetate } (90.8%) Fenchyl dichloracetate $Cl_2CH \cdot CO_2H$ (10% unreacted)	(133a)
1	Camphene <i>d</i> -Limonene		<i>d</i> - α -Pinene <i>d</i> -Dibornyl oxalate Diisobornyl oxalate } (26.6%) Difenchyl oxalate (8.65%) Tetrachloroethane	(133a)
1	Dipentene α -Terpinene		<i>dl</i> -Bornyl ester (over 15%)	(394)
1	Limonene	(trace)	α -Pinene (90%) Bornyl benzoate (3–5%)	(20)

Table 27. Isomerization of Bicyclenes and

Bicyclene	Reactants		Contact Time (hours)	Temp. (°C.)
	(Per cent by weight on bicyclene + catalyst)	Catalyst		
<i>l</i> - α -Pinene (French turpentine oil)	C ₆ H ₅ · CO ₂ H Cu vessel	(50%)	50	b.p.
<i>d</i> - α -Pinene	Salicylic acid	(27.8%)	60	130–135
<i>d</i> - α -Pinene	Salicylic acid	(33.3%)	50	130–135
<i>d</i> - α -Pinene	Salicylic acid	(50.0%)	50	130–135
<i>d</i> - α -Pinene	<i>o</i> -Benzoylbenzoic acid	(33.3%)	50	140
<i>l</i> - α -Pinene	Acetic anhydride B ₂ O ₃	(28.4%) (16.3%)	14	90–95
α -Pinene	Acetic anhydride B ₂ O ₃ CH ₃ · CO ₂ H	(7.2–10.3%) (0.68–1.3%) (36.3–43.2%)	15–28	110–120
<i>l</i> - α -Pinene	Acetic anhydride H ₃ BO ₃	(27.5–46.1%) (6.9–16.4%)	17–45	110–130
α -Pinene	Colophony	(66.7%)	6–7	163–165
<i>l</i> - α -Pinene (French turpentine oil)	C ₆ H ₅ OH	(25.7%)	5	160
<i>l</i> - α -Pinene (French turpentine oil)	C ₆ H ₅ OH	(40.8%)	5	160
<i>l</i> - α -Pinene (French turpentine oil)	C ₆ H ₅ OH	(58.0%)	5	160
<i>l</i> - α -Pinene (French turpentine oil)	<i>o</i> -Cresol	(16.6%)	5	160
<i>l</i> - α -Pinene (French turpentine oil)	Resorcinol		5	140
<i>l</i> - α -Pinene (French turpentine oil)	Neutral solvent			240
<i>l</i> - α -Pinene (French turpentine oil)	Methyl salicylate	(18.3%)	4	b.p. (?)
<i>l</i> - α -Pinene (French turpentine oil)	<i>p</i> -Nitrophenol		1	b.p.
<i>l</i> - α -Pinene (French turpentine oil)	<i>p</i> -Nitro- <i>m</i> -cresol			b.p. (?)
<i>l</i> - α -Pinene (French turpentine oil)	<i>m</i> -Dinitrophenol			b.p. (?)

Bicyclenes with Saturated Side-Chains—Continued

Pressure (atms.)	Isomers	Products (Per cent by weight on original bicyclene)		Refer- ences
		Isomers	Other Products	
1	<i>l</i> -Camphene <i>l</i> -Limonene	(10%) (33.3%)	<i>l</i> -Bornyl benzoate (<i>Ld</i>)-Fenchyl benzoate } (50%) Colophony	(76)
1	<i>d</i> -Limonene <i>l</i> -Limonene	(51.7%) (trace)	<i>d</i> - α -Pinene (8.3%) <i>d</i> -Bornyl salicylate } (49%) Isobornyl salicylate } Fenchyl salicylate } Salicylic acid (19% unreacted)	(133a)
1	<i>d</i> -Limonene <i>l</i> -Limonene	(trace)	<i>d</i> - α -Pinene <i>d</i> -Bornyl salicylate Isobornyl salicylate Fenchyl salicylate Salicylic acid (23% unreacted)	(133a)
1	Camphene Dipentene Terpinolene		<i>d</i> -Bornyl salicylate } (68%) Isobornyl salicylate } Fenchyl salicylate } Salicylic acid (56% unreacted) H ₂ O (trace) CO ₂ (trace)	(133a)
1	Camphene <i>d</i> -Limonene		<i>d</i> - α -Pinene <i>d</i> -Bornyl <i>o</i> -benzoyl- benzoate } (48.3%) Isobornyl <i>o</i> -benzoyl- benzoate } Fenchyl <i>o</i> -benzoyl- benzoate } <i>o</i> -Benzoylbenzoic acid (30% unreacted)	(133a)
1	<i>l</i> -Camphene Dipentene		<i>l</i> - α -Pinene Bornyl acetate Isobornyl acetate Fenchyl acetate	(268)
1	Camphene Dipentene α -Terpinene Terpinolene		α -Pinene <i>p</i> -Cymene Bornyl acetate Isobornyl acetate α -Fenchyl acetate (?) β -Fenchyl acetate (?)	(269)
1	<i>l</i> -Camphene Dipentene		<i>l</i> - α -Pinene <i>p</i> -Cymene Bornyl acetate Isobornyl acetate α -Fenchyl acetate β -Fenchyl acetate α -Terpinyl acetate (?) A diterpene acetate (?)	(268)
1	Camphene			(439)
1	<i>l</i> -Camphene		<i>l</i> - α -Pinene Phenol	(322)
1	<i>l</i> -Camphene		<i>l</i> - α -Pinene Phenol	(322)
1	<i>l</i> -Camphene		<i>l</i> - α -Pinene Phenol	(322)
1	<i>l</i> -Camphene		<i>l</i> - α -Pinene	(322)
1	<i>l</i> -Camphene		<i>l</i> - α -Pinene	(322)
4	<i>l</i> -Camphene		<i>l</i> - α -Pinene	(322)
1	Camphene	(small %)	Diterpene	(trace) (322)
1	Camphene		Diterpene <i>p</i> -Nitro- <i>m</i> -cresol	(322)
1	Camphene		Diterpene	(322)

Table 27. Isomerization of Bicyclenes and

Reactants		Catalyst (Per cent by weight on bicyclene + catalyst)	Contact Time (hours)	Temp. (°C.)
Bicyclene				
<i>l</i> - α -Pinene (French turpentine oil)	Dinitro- <i>o</i> -cresol			b.p. (?)
<i>l</i> - α -Pinene (French turpentine oil)	2,6-Dinitro- <i>p</i> -cresol			b.p. (?)
<i>l</i> - α -Pinene (French turpentine oil)	Picric acid	(20.0%)		135-b.p.
<i>d</i> - α -Pinene	Picric acid Benzene (solvent)	(13.3%) (20%)	0.5	120
<i>l</i> - α -Pinene (French turpentine oil)	Picric acid Toluene (solvent)		1	130-140
<i>l</i> - α -Pinene (French turpentine oil)	2,4,5-Trinitro- <i>m</i> -cresol Toluene (solvent)	(18-21%) (7-15%)		109
<i>l</i> - α -Pinene (French turpentine oil)	2,4,5-Trinitro- <i>m</i> -cresol			b.p. (?)
<i>l</i> - α -Pinene (French turpentine oil)	Trinitrothymol			b.p. (?)
<i>l</i> - α -Pinene (French turpentine oil)	Tribromophenol With or without toluene as solvent		1-50	120-240
<i>l</i> - α -Pinene (French turpentine oil)	Trichlorophenol	(6.75%)		b.p. (?)
<i>l</i> - α -Pinene (French turpentine oil)	Trichlorophenol Toluene (solvent)			b.p. (?)
<i>d</i> - Δ^3 -Carene	"Suprax" glass			400
<i>d</i> - Δ^4 -Carene			4	280
<i>d</i> - Δ^4 -Carene	CH ₃ . CO ₂ H			b.p.
<i>trans</i> -1,2,3,4,4a,5,8,8a-Octahydro- naphthalene (<i>trans</i> - Δ^2 -Octalin)	P ₂ O ₅		3	140

Bicyclenes with Saturated Side-Chains—Continued

Pressure (atms.)	Products		Refer- ences
	Isomers	Other Products	
1	Camphene	Diterpene	(322)
1	Camphene	Diterpene	(322)
1	<i>l</i> -Camphene	<i>l</i> - α -Pinene	(322)
	Dipentene	Diterpene	(18.4%) (3.7%)
		Bornyl picrate } Picric acid }	(30%)
		Borneol	(trace)
		H ₂ O	(trace)
1	<i>d</i> -Limonene	<i>d</i> -Bornyl picrate	(24%) (133)
	<i>d</i> -Camphene	<i>l</i> -Bornyl picrate	(trace)
	<i>d</i> - α -Pinene	Isobornyl picrate	(trace)
		<i>l</i> -Fenchyl picrate	
1	Camphene	<i>l</i> - α -Pinene	(trace) (322)
	Dipentene	Bornyl picrate	(trace)
		H ₂ O	(trace)
1	<i>l</i> -Camphene	<i>l</i> - α -Pinene	(322)
	Dipentene	2,4,5-Trinitro- <i>m</i> -cresol	
		Bornyl-2,4,5-trinitro- <i>m</i> - cresolate	(10–15%)
1	Camphene	Diterpene	(322)
	Dipentene	Bornyl-2,4,5-trinitro- <i>m</i> - cresolate	
1	Camphene	Diterpene	(322)
	Dipentene	Bornyl-trinitrothymolate	
1–4	Camphene	Diterpene	(trace) (322)
		Bornyl-tribromophenolate (?)	
1	Camphene	Diterpene	(322)
		Bornyl-trichlorophenolate (?)	
1	Camphene	Diterpene	(322)
		Bornyl-trichlorophenolate (?)	
	No isomers	<i>d</i> - Δ^3 -Carene unchanged	(12)
	Sylvestrene		(538)
	α -Terpinene		
1	α -Terpinene		(538)
1	1,2,3,4,5,6,7,8-Octahydro- naphthalene		(353)

Table 28. Isomerization of Bicyclenes

Bicyclene	Reactants (Per cent by weight on bicyclene + catalyst)	Catalyst	Contact Time (hours)	Temp. (°C.)
Caryophyllene (b.p. 123–124° at 16 mm. Hg)	H ₂ SO ₄ (C ₂ H ₅) ₂ O Later, NaOH solution	(28%) (21%)	10 at then “overnight” at then alkali at	0–10 room 0 100 (?)
Caryophyllene	H ₂ SO ₄ CH ₃ . CO ₂ H			
Caryophyllene	H ₂ SO ₄ , H ₂ O, CH ₃ . CO ₂ H, 94.34%	1.89% 3.77% (77%?)	12 (?)	100 (?)
β-Caryophyllene	H . CO ₂ H	(50% by vol.)	several days	b.p.
d-α-Selinene	H ₂ SO ₄ C ₂ H ₅ OH	(9.8%) (77.2%)	several	b.p.
Sclarene	H . CO ₂ H	(72.2%)	4	120

Table 29. Isomerization of Bicyclodienes

Bicyclodiene	Reactants (Per cent by weight on bicyclodiene + catalyst)	Catalyst	Contact Time (hours)	Temp. (°C.)
l-Cadinene (regenerated)			12 (?)	330
l-Cadinene	Dilute H ₂ SO ₄		several	heated
Cadinene	H ₂ SO ₄ , 57% H ₂ O, 43% “30% H ₂ SO ₄ ”	(98.8%) (4.4%)	36	b.p.
l-Cadinene (regenerated)	CH ₃ . CO ₂ H	(93.8%)	8	100
l-Cadinene (regenerated)	CH ₃ . CO ₂ H	(25%)	24	230–235°

Table 30. Isomerization of Tricyclenes and

Tricyclene	Reactants (Per cent by weight on tricyclene + catalyst)	Catalyst	Contact Time (hours)	Temp. (°C.)
Δ ^{11,12} -Dodecahydrophenanthrene				b.p.
Cedrene	H . CO ₂ H	(50% by ? vol.)	several days (?)	b.p.
l-α-Gurjunene (l-Tricyclene-gurjunene)			12	330
l-α-Gurjunene	H ₂ SO ₄ CH ₃ . CO ₂ H	(6.9%) (58.7%)	2	100
d-β-Gurjunene (d-Tricyclo-gurjunene)	HCl (gas) CH ₃ . CO ₂ H	(67.7%)		room
l-Sesquichamene	H ₂ SO ₄ C ₂ H ₅ OH	(14.3%) (14.3%)	1.5	40–50

with Unsaturated Side-Chains

Pressure (atms.)	Products			Refer- ences
	Isomers	(Per cent by weight on original bicycene)	Other Products	
1	Clovene	(8.5%)	α -Iso-caryophyllene alcohol (2%)	(488)
1			β -Iso-caryophyllene alcohol (25%)	
1				
1 (?)	<i>l</i> -Isomer (b.p. 126–127° at 24 mm. Hg)		"Caryophyllene alcohol"	(136)
1 (?)	<i>l</i> -Isomer (b.p. 126–127° at 24 mm. Hg)		"Isocaryophyllene alcohol"	(137)
	<i>l</i> -Isomer (b.p. 126–130° at 18 mm. Hg) ("Clovene")			
1	Clovene		Caryophyllene Formate of "caryophyllene alcohol" (35%)	(469)
1	<i>d</i> - δ -Selinene (?)			(492)
	<i>d</i> - ϵ -Selinene (?)			
1	Tricyclic isomer	(42%)	Sclarene	(489)

with Saturated Side-Chains

Pressure (atms.)	Products			Refer- ences
	Isomers	(Per cent by weight on original bicyclodiene)	Other Products	
bomb	<i>l</i> -Monocyclic isomer		Cadinene	(536)
	Isomer			(633)
1	Isomer (b.p. 140–145° at 12 mm. Hg)			(493)
1	Isocadinene			(246)
bomb	Isocadinene			(246)

Tricyclenes with Saturated Side-Chains

Pressure atms.	Products			Refer- ences
	Isomers	(Per cent by weight on original tricycene)	Other Products	
10–26 mm. Hg	$\Delta^{12,13}$ -Dodecahydro-phenanthrene		Octahydrophenanthrene	(150)
1	Tricyclic isomer	(50%)	Tetradecahydrophenanthrene	(469)
			Cedrene	
bomb	<i>dl</i> - α -Gurjunene		"Alcoholic substances"	
			C ₁₀ H ₁₆	(536)
1	<i>l</i> -Iso- α -gurjunene		C ₂₀ H ₃₂	(591)
			Polymers	
1	<i>l</i> -Iso- β -gurjunene			(591)
1	<i>l</i> -Isosquichamene			(294)

Table 31. Isomerization of Tricyclenes

Tricyclene	Reactants (Per cent by weight on tricyclene + catalyst)	Catalyst (Per cent by weight on tricyclene + catalyst)	Contact Time (hours) (heating and cooling period)	Temp. (°C.) b.p.
<i>d</i> -Rimuenene				
<i>d</i> -Rimuenene		H . CO ₂ H, 90% H ₂ O, 10%	48	

Table 32. Isomeriza

Tetracyclene	Reactants (Per cent by weight on tetracyclene + catalyst)	Catalyst (Per cent by weight on tetracyclene + catalyst)	Contact Time (hours)	Temp. (°C.)
<i>d</i> -2,4-Cholestadiene	Conc. HCl	(2%)	6-26	b.p.
<i>d</i> -4,6-Cholestadiene	"95% C ₂ H ₅ OH"	(96%)	3	0
Phyllocladene (Dacrene)	CHCl ₃ (solvent)	(91.1%)		
Phyllocladene (Dacrene)	HCl (gas)	(to saturation)		
Phyllocladene	SiO ₂ tube			800-900 room
Phyllocladene	HNO ₃			
Phyllocladene	Light petroleum (diluent)			
Phyllocladene	H ₂ SO ₄ , 10% C ₂ H ₅ OH, 90%			b.p.
<i>d</i> -Phyllocladene (<i>d</i> -Sciadopitene)	H ₂ SO ₄ , 10% C ₂ H ₅ OH, 90%		5	b.p.
Phyllocladene	H ₂ SO ₄ , 10% C ₂ H ₅ OH, 90%		few minutes	100
Phyllocladene (Dacrene)	K ₂ Cr ₂ O ₇			
Phyllocladene (Dacrene)	CH ₃ . CO ₂ H		"short time"	b.p.
Phyllocladene (Dacrene)	H . CO ₂ H, 90% H ₂ O, 10%		"short time"	b.p.
Phyllocladene (Dacrene)	CH ₃ . CO ₂ H			

Table 33. Isomeriza

Pentacyclene	Reactants (Per cent by weight on pentacyclene + catalyst)	Catalyst (Per cent by weight on pentacyclene + catalyst)	Contact Time (hours)	Temp. (°C.)
<i>d</i> -17,18- <i>cis</i> - $\Delta^{12,13}$ (?) -Oleanene	CH ₃ . CO ₂ H	(65.6%?)	6	b.p.
	Amalgamated zinc wool	(15.6%?)		
	Hydrochloric acid	(18.6%?)		
<i>d</i> -17,18- <i>trans</i> - $\Delta^{12,13}$ (?) -Oleanene	CH ₃ . CO ₂ H	(65.6%)	4	b.p.
	Amalgamated zinc wool	(15.6%)		
	Hydrochloric acid	(18.6%)		

Table 35. Isomerization of Benzenes

Substituted Benzene	Reactants	Catalyst (Per cent by weight on aromatic + catalyst)	Contact Time (hours)	Temp. (°C.)
Toluene	Ultraviolet light (?)			67
1,2-Dimethylbenzene (<i>o</i> -Xylene)	Porcelain tube used		2 g. feed per 353.4 ml. zone per minute	700
1,2-Dimethylbenzene	Porcelain tube used		2 g. feed per 353.4 ml. zone per minute	730
1,2-Dimethylbenzene	Porcelain tube used		2 g. feed per 353.4 ml. zone per minute	750
1,2-Dimethylbenzene	Porcelain tube used		2 g. feed per 353.4 ml. zone per minute	770
1,2-Dimethylbenzene	AlCl ₃ HCl (gas)	(55.7%)	5	50
1,2-Dimethylbenzene	AlCl ₃ HCl (gas)	(56%)	10 min.	55
1,2-Dimethylbenzene	AlCl ₃ HCl (gas)	(55.7%)	0.25	94
1,2-Dimethylbenzene	AlCl ₃	(16.7%)	6	100
1,3-Dimethylbenzene (<i>m</i> -Xylene)	Quartz tube used		15 ml. feed per 219.3 ml. zone per hour	800
1,3-Dimethylbenzene	AlCl ₃			
1,3-Dimethylbenzene	AlCl ₃ HCl (gas)	(55.7%)	0.5	50
1,3-Dimethylbenzene	AlCl ₃ HCl (gas)	(55.7%)	1.5	50
1,3-Dimethylbenzene	AlCl ₃ HCl (gas)	(55.7%)	5	50
1,3-Dimethylbenzene	AlCl ₃ HCl (gas)	(55.7%)	18	50
1,3-Dimethylbenzene	AlCl ₃ FeCl ₃ HCl	(26.3%) (32%)	20	50
1,3-Dimethylbenzene	AlCl ₃ FeCl ₃ HCl	(55%) (2%)	20	50

with Saturated Side-Chains

Pressure (atms.)	Products (Per cent by weight on original aromatic)			Refer- ences
	Isomers	Other Products		
1	1-Methylenecyclohexadiene-3,5	Toluene		(376)
	1,3-Dimethylbenzene (4.0%)	Gas	(2.1%)	(139)
	1,4-Dimethylbenzene (trace)	Toluene	(4.6%)	
1		1,2-Dimethylbenzene	(76.3%)	
		Condensed products	(12.1%)	
	1,3-Dimethylbenzene (6.5%)	Gas	(4.3%)	(139)
1	1,4-Dimethylbenzene (1.4%)	Toluene	(8.2%)	
		1,2-Dimethylbenzene	(59.9%)	
		Condensed products	(3.6%)	
1	1,3-Dimethylbenzene (10.9%)	Gas	(8.9%)	(139)
	1,4-Dimethylbenzene (3.5%)	Toluene	(11.5%)	
		1,2-Dimethylbenzene	(38.7%)	
1		Condensed products	(24.8%)	
	1,3-Dimethylbenzene (16.8%)	Gas	(14.8%)	(139)
	1,4-Dimethylbenzene (4.6%)	Toluene	(2.8%)	
1		1,2-Dimethylbenzene	(22.5%)	
		Condensed products	(25.4%)	
	1,3-Dimethylbenzene (below 51.7%)	1,2-Dimethylbenzene	(below 37.6%)	(415)
1	1,4-Dimethylbenzene (below 4.7%)			
	1,3-Dimethylbenzene (18.7%)	1,2-Dimethylbenzene	(81.6%)	(414)
1	1,3-Dimethylbenzene (below 38.6%)	1,2-Dimethylbenzene	(below 31.9%)	(415)
	1,4-Dimethylbenzene (below 13.4%)			
	1,2-Dimethylbenzene	Benzene (?)	(2%)	(245)
1	1,3-Dimethylbenzene (mainly)	Pseudocumene (mainly)	(5%)	
	1,4-Dimethylbenzene	Mesitylene		
	No 1,4-dimethylbenzene found	Tar		
1		Benzene	(1.5%)	(28)
		Toluene	(22.1%)	
		Xylene of b.p. 135°	(23.5%)	
1		Naphthalene, anthracene, and other residues	(17.6%)	
	1,4-Dimethylbenzene	Benzene		(7)
		Toluene		
1		Mesitylene		
		Pseudocumene		
		Durene		
1	1,4-Dimethylbenzene (2.8%)	Isodurene		
		1,3-Dimethylbenzene	(89.2%?)	(415)
1	1,2-Dimethylbenzene (15%)	1,3-Dimethylbenzene	(72.4%)	(415)
	1,4-Dimethylbenzene (6.6%)			
1	1,2-Dimethylbenzene (11.7%)	1,3-Dimethylbenzene	(61.9%)	(415)
	1,4-Dimethylbenzene (10%)			
1	1,2-Dimethylbenzene (12.9%)	1,3-Dimethylbenzene	(55.7%)	(415)
	1,4-Dimethylbenzene (12.1%)			
1	1,2-Dimethylbenzene (below 17%)	1,3-Dimethylbenzene	(below 68%)	(415)
	1,4-Dimethylbenzene (below 15%)			
1	1,2-Dimethylbenzene (below 16%)	1,3-Dimethylbenzene	(below 69%)	(415)
	1,4-Dimethylbenzene (below 15%)			

Table 35. Isomerization of Benzenes

Substituted Benzene	Reactants (Per cent by weight on aromatic + catalyst)	Catalyst	Contact Time (hours)	Temp. (°C.)
1,3-Dimethylbenzene	AlCl ₃ HCl	(55.7%)	20	50
1,3-Dimethylbenzene	AlCl ₃ HCl	(55.7%)	30	50
1,3-Dimethylbenzene	AlCl ₃ HCl	(1.24%)	48	50
1,3-Dimethylbenzene	AlCl ₃ HCl	(20.1%)	48	50
1,3-Dimethylbenzene	AlCl ₃ HCl	(55.7%)	48	50
1,3-Dimethylbenzene	AlCl ₃	(55.7%)	50	50
1,3-Dimethylbenzene	AlCl ₃ HCl	(55.7%)	50	50
1,3-Dimethylbenzene	AlCl ₃ HCl	(55.7%)	75	50
1,3-Dimethylbenzene	AlCl ₃ HCl	(55.7%)	0.25	94
1,3-Dimethylbenzene	AlCl ₃ HCl (gas)		6	100
1,3-Dimethylbenzene	AlCl ₃	(20–25%)		b.p.
1,4-Dimethylbenzene (<i>p</i> -Xylene)	Porcelain tube used		2 g. feed per 353.4 ml. zone per minute	700
1,4-Dimethylbenzene	Porcelain tube used		2 g. feed per 353.4 ml. zone per minute	730
1,4-Dimethylbenzene	Porcelain tube used		2 g. feed per 353.4 ml. zone per minute	750
1,4-Dimethylbenzene	Porcelain tube used		2 g. feed per 353.4 ml. zone per minute	770
1,4-Dimethylbenzene	Quartz tube used		15 ml. feed per 219.3 ml. zone per hour	800

with Saturated Side-Chains—*Continued*

Pressure (atms.)	Products (Per cent by weight on original aromatic)		Refer- ences (415)
	Isomers	Other Products	
1	1,2-Dimethylbenzene (below 16%)	1,3-Dimethylbenzene (below 69%)	
	1,4-Dimethylbenzene (below 15%)		
1	1,2-Dimethylbenzene (12.5%)	1,3-Dimethylbenzene (53.9%)	(415)
	1,4-Dimethylbenzene (12.1%)		
1	1,4-Dimethylbenzene (below 4%)	1,3-Dimethylbenzene (below 96%)	(415)
1	1,2-Dimethylbenzene (below 11.7%)	1,3-Dimethylbenzene (below 61.2%)	(415)
	1,4-Dimethylbenzene (below 17.1%)		
1	1,2-Dimethylbenzene (11.1%)	1,3-Dimethylbenzene (46.6%)	(415)
	1,4-Dimethylbenzene (11.8%)		
1	1,2-Dimethylbenzene (below 13.4%)	1,3-Dimethylbenzene (below 68.2%)	(415)
	1,4-Dimethylbenzene (below 14.4%)		
1	1,2-Dimethylbenzene (below 12.8%)	1,3-Dimethylbenzene (below 53.6%)	(415)
	1,4-Dimethylbenzene (below 14.4%)		
1	1,2-Dimethylbenzene (10.2%)	1,3-Dimethylbenzene (41.7%)	(415)
	1,4-Dimethylbenzene (12.2%)		
1	1,2-Dimethylbenzene (below 18%)	1,3-Dimethylbenzene (below 72%)	(415)
	1,4-Dimethylbenzene (below 10%)		
1	1,3-Dimethylbenzene (mainly), } (78.6%)	Low-boiling hydrocarbon (2.86%)	(245)
	1,4-Dimethylbenzene } (33.3%)	Mesitylene (mainly), { (5.7%)	
1	1,3-Dimethylbenzene (mainly), } (33.3%)	Pseudocumene { (1.67%)	(6)
	1,4-Dimethylbenzene } (33.3%)	Benzene (20.8%)	
		Toluene, crude (20.8%)	
		Mesitylene (mainly), { (20.8%)	
		Pseudocumene { (5%)	
		Durene	
		Tetramethylanthracene (m.p. 290°)	(0.083%)
1	1,3-Dimethylbenzene (1.2%)	Gas (0.9%)	(139)
		Toluene (2.1%)	
		1,4-Dimethylbenzene (88.2%)	
		Condensed products (6.9%)	
1	1,3-Dimethylbenzene (3.7%)	Gas (3.7%)	(139)
		Toluene (4.6%)	
		1,4-Dimethylbenzene (73.1%)	
		Condensed products (14.1%)	
1	1,3-Dimethylbenzene (4.1%)	Gas (8.9%)	(139)
		Toluene (7.9%)	
		1,4-Dimethylbenzene (57.3%)	
		Condensed products (17.8%)	
1	1,3-Dimethylbenzene (3.8%)	Gas (14.8%)	(139)
		Toluene (13.3%)	
		1,4-Dimethylbenzene (45.4%)	
		Condensed products (19.3%)	
1	1,3-Dimethylbenzene, crude (3.3%)	Gas	(28)
		Benzene (3.3%)	
		Toluene (22%)	
		1,4-Dimethylbenzene (23.3%)	
		2,6-Dimethylanthracene and other residues (22%)	

Table 35. Isomerization of Benzenes

Substituted Benzene	Reactants (Per cent by weight on aromatic + catalyst)	Catalyst	Contact Time (hours)	Temp. (°C.)
1,4-Dimethylbenzene	AlCl ₃ HCl (gas)	(55.5%)	5	40-50
1,4-Dimethylbenzene	AlCl ₃ HCl (gas)	(55.7%)	5	50
1,4-Dimethylbenzene	AlCl ₃ HCl (gas)	(56%)	10 min.	55
1,4-Dimethylbenzene	AlCl ₃ HCl (gas)	(55.7%)	0.25	94
1,4-Dimethylbenzene	AlCl ₃ HCl (gas)	(16.7%)	6	100
Ethylbenzene	Porcelain tube used		(long)	moderate red-heat
Ethylbenzene	Porcelain tube used			moderate red-heat
1,2,4-Trimethylbenzene (Pseudocumene)	AlCl ₃			
1,2,4-Trimethylbenzene	AlCl ₃	(7.4%)	6	150-160
1,2,4-Trimethylbenzene	AlCl ₃	(21.2%)	2	b.p.
1,3,5-Trimethylbenzene (Mesitylene)	AlCl ₃ HCl (gas)	(9.1%)	4	150-160
1,2,3,5-Tetramethylbenzene (Isodurene)	H ₂ SO ₄ (sulfonation) Later, hydrolysis of prehnitene sulfonic acid dihydrate at 140- 150° by dilute H ₂ SO ₄ and superheated steam	(78.6%)	10 days	at room (sulfona- tion)

with Saturated Side-Chains—Continued

Pressure (atms.)	Products (Per cent by weight on original aromatic)		Refer- ences (392)
	Isomers	Other Products	
1	1,3-Dimethylbenzene		(415)
1	1,2-Dimethylbenzene (below 11.6%)	1,4-Dimethylbenzene (below 8.3%)	
	1,3-Dimethylbenzene (below 63.1%)		
1	1,2-Dimethylbenzene (0.6%)	1,4-Dimethylbenzene (35.1%)	(414)
	1,3-Dimethylbenzene (64.3%)		
1	1,2-Dimethylbenzene (below 14.4%)	1,4-Dimethylbenzene (below 47.7%)	(415)
	1,3-Dimethylbenzene (below 27.9%)		
1	1,3-Dimethylbenzene (50%)	Benzene (2%?)	(245)
		Mesitylene (5%?)	
		Pseudocumene	(63)
	1,4-Dimethylbenzene	Benzene	
		Toluene	
		Ethylbenzene	
		Styrene (large %)	
		Naphthalene	
		Dihydronaphthalene	(61)
	1,4-Dimethylbenzene	Benzene	
		Toluene	
		Ethylbenzene (?)	
		Styrene (large %)	
		Phenylethyne	
		Naphthalene	
		Dihydronaphthalene	(7)
	1,3,5-Trimethylbenzene	Benzene	
		Toluene	
		1,4-Dimethylbenzene	
		Durene	
		Isodurene	(290)
1	1,3,5-Trimethylbenzene (3.2–4%)	HCl	
		CH ₃ Cl	
		Benzene (2%)	
		Toluene (8%)	
		<i>m</i> -Xylene (mainly), } (26–28%)	
		<i>p</i> -Xylene (8%)	
		Durene (3.2%)	
		Isodurene (15.4%)	(6)
1	1,3,5-Trimethylbenzene (30.8%)	Toluene	
		<i>m</i> -Xylene (mainly), } (15.4%)	
		<i>p</i> -Xylene	
		Isodurene (mainly), } (11.5%)	
		Durene (small %)	
		Anthracenes	(290)
1	1,2,4-Trimethylbenzene (small %)	CH ₃ Cl	
		Benzene (small %)	
		Toluene (small %)	
		<i>m</i> -Xylene (large %)	
		Durene (5%)	
		Isodurene (16%)	
1	1,2,3,4-Tetramethylbenzene (yield of sulfonic acid dihydrate was 50% of theory)	SO ₂ (during sulfonation)	(558)

Table 35. Isomerization of Benzenes

Substituted Benzene	Reactants		Contact Time (hours)	Temp. (°C.)
	Catalyst (Per cent by weight on aromatic + catalyst)			
1,2,4,5-Tetramethylbenzene (Durene)	H ₂ SO ₄ (sulfonation) (78.6%) Later, hydrolysis of prehnitene sulfonic acid dihydrate at 140– 150° by dilute H ₂ SO ₄ and superheated steam		25 days	at room (sulfona- tion)
<i>sec</i> -Butylbenzene	AlCl ₃	(20%)	4	140–145
“1,3-Dimethyl-4- <i>n</i> -propyl- benzene”	AlCl ₃	(20%)	4	100
“1,3-Dimethyl-4-isopropyl- benzene”	AlCl ₃	(17.9%)	3	55–60
1,2,4-Trimethyl-5-ethyl- benzene	H ₂ SO ₄ + 10% SO ₃ (85%) Later, “50% H ₂ SO ₄ ” + steam (hydrolysis)		1 (sulfonation)	60–70 (sulfon- ation) 140–150 (hydrol- ysis)
1,3,5-Trimethyl-2-ethylbenzene	H ₂ SO ₄ + 10% SO ₃ (85%) Later, “50% H ₂ SO ₄ ” + steam (hydrolysis)		6 (sulfonation)	60–70 (sulfon- ation) 140–150 (hydrol- ysis)
“1,3-Dimethyl-4- <i>n</i> -butylbenzene”	AlCl ₃	(17.8%)	4	100
“1,3-Dimethyl-4- <i>n</i> -butyl- benzene”	FeCl ₃ (anhydrous)	(20.1%)	2.25	80–100
“1,3-Dimethyl-4-isobutyl- benzene”	FeCl ₃ (anhydrous)	(20.4%)	2.25	80–100
“1,3-Dimethyl-4- <i>sec</i> -butyl- benzene”	AlCl ₃	(17.8%)	2.5	100
“1,3-Dimethyl-4- <i>sec</i> -butyl- benzene”	FeCl ₃ (anhydrous)	(20.1%)	1.5	80
“1,3-Dimethyl-4- <i>tert</i> -butyl- benzene”	AlCl ₃	(17.24%)	3.25	100

with Contained Side-Chainswith Contained Side-Chainswith Contained Side-Chainswith Contained Side-Chains

Products	Products	Products	Products
on original sample by weight on original sample by weight on original sample by weight on original sample by weight	on original sample by weight on original sample by weight on original sample by weight on original sample by weight	on original sample by weight on original sample by weight on original sample by weight on original sample by weight	on original sample by weight on original sample by weight on original sample by weight on original sample by weight
Residual Products	Residual Products	Residual Products	Residual Products
(55%)	(55%)	(55%)	(55%)
Tetrahydronaphthalene (1,2,3,4-tetrahydronaphthalene) (yield of sulfonic acid dihydrate was 70% of theory)	Tetrahydronaphthalene (1,2,3,4-tetrahydronaphthalene) (yield of sulfonic acid dihydrate was 70% of theory)	Tetrahydronaphthalene (1,2,3,4-tetrahydronaphthalene) (yield of sulfonic acid dihydrate was 70% of theory)	Tetrahydronaphthalene (1,2,3,4-tetrahydronaphthalene) (yield of sulfonic acid dihydrate was 70% of theory)

Products, b.p. 120–150°	Products, b.p. 120–150°	Products, b.p. 120–150°	Products, b.p. 120–150°
Investigated	Investigated	Investigated	Investigated
1,3-Dimethyl-2-propylbenzene (crude, 23.9%)	1,3-Dimethyl-2-propylbenzene (crude, 23.9%)	1,3-Dimethyl-2-propylbenzene (crude, 23.9%)	1,3-Dimethyl-2-propylbenzene (crude, 23.9%)
1,3-Dimethyl-2-propylbenzene (90.6%)	1,3-Dimethyl-2-propylbenzene (90.6%)	1,3-Dimethyl-2-propylbenzene (90.6%)	1,3-Dimethyl-2-propylbenzene (90.6%)
1,2,4-Trimethyl-3-ethylbenzene (559)	1,2,4-Trimethyl-3-ethylbenzene (559)	1,2,4-Trimethyl-3-ethylbenzene (559)	1,2,4-Trimethyl-3-ethylbenzene (559)
1,2,4-Trimethyl-3-ethylbenzene (27.0%)	1,2,4-Trimethyl-3-ethylbenzene (27.0%)	1,2,4-Trimethyl-3-ethylbenzene (27.0%)	1,2,4-Trimethyl-3-ethylbenzene (27.0%)
1-Ethyl-2,4-dimethylbenzene (9.9%)	1-Ethyl-2,4-dimethylbenzene (9.9%)	1-Ethyl-2,4-dimethylbenzene (9.9%)	1-Ethyl-2,4-dimethylbenzene (9.9%)
1-Methyl-2,4-dimethylbenzene (7.0%)	1-Methyl-2,4-dimethylbenzene (7.0%)	1-Methyl-2,4-dimethylbenzene (7.0%)	1-Methyl-2,4-dimethylbenzene (7.0%)
Hydrocarbon, m.p. 173–175°	Hydrocarbon, m.p. 173–175°	Hydrocarbon, m.p. 173–175°	Hydrocarbon, m.p. 173–175°
Polymers	Polymers	Polymers	Polymers
1,2,4-Trimethyl-3-ethylbenzene (559)	1,2,4-Trimethyl-3-ethylbenzene (559)	1,2,4-Trimethyl-3-ethylbenzene (559)	1,2,4-Trimethyl-3-ethylbenzene (559)
1,2,4-Trimethyl-3-ethylbenzene (34.5%)	1,2,4-Trimethyl-3-ethylbenzene (34.5%)	1,2,4-Trimethyl-3-ethylbenzene (34.5%)	1,2,4-Trimethyl-3-ethylbenzene (34.5%)
1,3-Dimethyl-2-ethylbenzene (9.5%)	1,3-Dimethyl-2-ethylbenzene (9.5%)	1,3-Dimethyl-2-ethylbenzene (9.5%)	1,3-Dimethyl-2-ethylbenzene (9.5%)
1-Methyl-2-ethylbenzene (10.0%)	1-Methyl-2-ethylbenzene (10.0%)	1-Methyl-2-ethylbenzene (10.0%)	1-Methyl-2-ethylbenzene (10.0%)
Hydrocarbon, m.p. 185–188°	Hydrocarbon, m.p. 185–188°	Hydrocarbon, m.p. 185–188°	Hydrocarbon, m.p. 185–188°
Polymers	Polymers	Polymers	Polymers
1,3-Dimethyl-2-propylbenzene (405)	1,3-Dimethyl-2-propylbenzene (405)	1,3-Dimethyl-2-propylbenzene (405)	1,3-Dimethyl-2-propylbenzene (405)
Fraction, b.p. 50–105° at 16 mm. Hg	Fraction, b.p. 50–105° at 16 mm. Hg	Fraction, b.p. 50–105° at 16 mm. Hg	Fraction, b.p. 50–105° at 16 mm. Hg
Fraction, b.p. 105–145° at 16 mm. Hg	Fraction, b.p. 105–145° at 16 mm. Hg	Fraction, b.p. 105–145° at 16 mm. Hg	Fraction, b.p. 105–145° at 16 mm. Hg
Fraction, b.p. 85–91° at 16 mm. Hg	Fraction, b.p. 85–91° at 16 mm. Hg	Fraction, b.p. 85–91° at 16 mm. Hg	Fraction, b.p. 85–91° at 16 mm. Hg
Fraction, b.p. 94–105° at 26 mm. Hg	Fraction, b.p. 94–105° at 26 mm. Hg	Fraction, b.p. 94–105° at 26 mm. Hg	Fraction, b.p. 94–105° at 26 mm. Hg
Fraction, b.p. above 105° at 17 mm. Hg	Fraction, b.p. above 105° at 17 mm. Hg	Fraction, b.p. above 105° at 17 mm. Hg	Fraction, b.p. above 105° at 17 mm. Hg
Fraction, b.p. 85–91° at 16 mm. Hg	Fraction, b.p. 85–91° at 16 mm. Hg	Fraction, b.p. 85–91° at 16 mm. Hg	Fraction, b.p. 85–91° at 16 mm. Hg
Fraction, b.p. 94–105° at 26 mm. Hg	Fraction, b.p. 94–105° at 26 mm. Hg	Fraction, b.p. 94–105° at 26 mm. Hg	Fraction, b.p. 94–105° at 26 mm. Hg
Fraction, b.p. above 105° at 22 mm. Hg	Fraction, b.p. above 105° at 22 mm. Hg	Fraction, b.p. above 105° at 22 mm. Hg	Fraction, b.p. above 105° at 22 mm. Hg
1,3-Dimethyl-2-propylbenzene (405)	1,3-Dimethyl-2-propylbenzene (405)	1,3-Dimethyl-2-propylbenzene (405)	1,3-Dimethyl-2-propylbenzene (405)
Fraction, b.p. 44–145° at 2.7 mm. Hg	Fraction, b.p. 44–145° at 2.7 mm. Hg	Fraction, b.p. 44–145° at 2.7 mm. Hg	Fraction, b.p. 44–145° at 2.7 mm. Hg
Fraction, b.p. 91–145° at 2.7 mm. Hg	Fraction, b.p. 91–145° at 2.7 mm. Hg	Fraction, b.p. 91–145° at 2.7 mm. Hg	Fraction, b.p. 91–145° at 2.7 mm. Hg

Table 35. Isomerization of Benzenes

Substitute Benzene	Reactants		Contact Time (hours)	Temp. (°C.)
	(Per cent by weight on aromatic	Catalyst + catalyst)		
"1,3-Dimethyl-4- <i>tert</i> -butylbenzene"	AlCl ₃	(14.3%)	2	100
"1,3-Dimethyl-4- <i>tert</i> -butylbenzene"	FeCl ₃ (anhydrous)	(20.2%)	1.5	80
1,3-Dipropylbenzene	AlCl ₃	(25.3%)	22	100
1,4-Dipropylbenzene	AlCl ₃		2	100
1,4-Dipropylbenzene	AlCl ₃	(25.3%)	22	100
1,2,3,5-Tetraethylbenzene	H ₂ SO ₄ (sulfonation) Later, hydrolysis of the resultant sulfonic acid monohydrate at 140° by dilute H ₂ SO ₄ (50% by volume) and steam		15 min.	at 100 (sulfo- nation)
1,2,4,5-Tetraethylbenzene	H ₂ SO ₄ (sulfonation) Later, hydrolysis of the resultant sulfonic acid monohydrate at 140° by dilute H ₂ SO ₄ (50% by volume) and steam		15 min.	at 100 (sulfo- nation)
1,2,3,5-Tetraethylbenzene 1,2,4,5-Tetraethylbenzene (various mixtures)	H ₂ SO ₄ (sulfonation) (80%) Later, hydrolysis of the resultant 1,2,3,4-tetraethylbenzene sulfonic acid monohydrate (84 grams) at 130–150° by "50 per cent H ₂ SO ₄ " (300 cc.) and steam		15 min.	at 100 (sulfo- nation)
1,2,4-Tripropylbenzene	AlCl ₃		4	100
Hexaphenylethane	HCl (gas) Benzene (solvent)			
Hexaphenylethane	HCl (aqueous) Benzene (solvent)			
Hexaphenylethane ("Triphenylmethyl")	<i>m</i> -Xylene (solvent)			heated
Hexaphenylethane ("Triphenylmethyl")	Na Ether (solvent)			room
<i>dl</i> -2,3-Diphenylbutane			8	235–250
<i>dl</i> -3,4-Diphenylhexane	I ₂			250–265
<i>meso</i> -3,4-Diphenylhexane	I ₂			250–265

ainswith Continued Side-Chainswith Continued Side-Chainswith Continued Side-Cha

Products
on original amount by weight, on original amount by weight, on original amount by weight, on original amount by weight

Fraction (99.1%) 40-100° at 13-Dimethylbenzene (45%) Fraction, b.p. 105-115 (5.5%) Fraction (40.5%) 35-91° at 13-Dimethylbenzene (68%) Fraction, b.p. 93-97 at (13.3%) Fraction, b.p. above 97° (10%) 1,2,3,4-Tetraethylbenzene (over 85%)	Fraction (99.1%) 40-100° at 13-Dimethylbenzene (45%) Fraction, b.p. 105-115 (5.5%) Fraction (40.5%) 35-91° at 13-Dimethylbenzene (68%) Fraction, b.p. 93-97 at (13.3%) Fraction, b.p. above 97° (10%) 1,2,3,4-Tetraethylbenzene (over 85%)	Fraction (99.1%) 40-100° at 13-Dimethylbenzene (45%) Fraction, b.p. 105-115 (5.5%) Fraction (40.5%) 35-91° at 13-Dimethylbenzene (68%) Fraction, b.p. 93-97 at (13.3%) Fraction, b.p. above 97° (10%) 1,2,3,4-Tetraethylbenzene (over 85%)	Fraction (99.1%) 40-100° at 13-Dimethylbenzene (45%) Fraction, b.p. 105-115 (5.5%) Fraction (40.5%) 35-91° at 13-Dimethylbenzene (68%) Fraction, b.p. 93-97 at (13.3%) Fraction, b.p. above 97° (10%) 1,2,3,4-Tetraethylbenzene (over 85%)
---	---	---	---

1-Tetraethylbenzene (558a) (over 85%)	1,2,3,4-Tetraethylbenzene (558a) (over 85%)	1,2,3,4-Tetraethylbenzene (558a) (over 85%)	1,2,3,4-Tetraethylbenzene (558a) (over 85%)
---------------------------------------	---	---	---

1-Tetraethylbenzene (558a) (81-83%)	1,2,3,4-Tetraethylbenzene (558a) (81-83%)	1,2,3,4-Tetraethylbenzene (558a) (81-83%)	1,2,3,4-Tetraethylbenzene (558a) (81-83%)
-------------------------------------	---	---	---

Tripropylbenzene (37) (60% (mainly),	Tripropylbenzene (37) (60% (mainly),	Tripropylbenzene (37) (60% (mainly),	Tripropylbenzene (37) (60% (mainly),
--------------------------------------	--------------------------------------	--------------------------------------	--------------------------------------

1,4-Dipropylbenzene (12%)	1,4-Dipropylbenzene (12%)	1,4-Dipropylbenzene (12%)	1,4-Dipropylbenzene (12%)
---------------------------	---------------------------	---------------------------	---------------------------

Benzohydryl-tetraphenyl-p-Benzohydryl-tetraphenyl-p-Benzohydryl-tetraphenyl-p-Benzohydryl-tetraphenyl-p-Ber	methane (222)	methane (222)	methane (222)
---	---------------	---------------	---------------

Benzohydryl-tetraphenyl-p-Benzohydryl-tetraphenyl-p-Benzohydryl-tetraphenyl-p-Benzohydryl-tetraphenyl-p-Ber	methane (222)	methane (222)	methane (222)
---	---------------	---------------	---------------

Benzohydryl-tetraphenyl-p-Benzohydryl-tetraphenyl-p-Benzohydryl-tetraphenyl-p-Benzohydryl-tetraphenyl-p-Ber	methane (222)	methane (222)	methane (222)
---	---------------	---------------	---------------

Benzohydryl-tetraphenyl-p-Benzohydryl-tetraphenyl-p-Benzohydryl-tetraphenyl-p-Benzohydryl-tetraphenyl-p-Ber	methane (222)	methane (222)	methane (222)
---	---------------	---------------	---------------

2,3-Diphenylbutane (N ₂)	meso-2,3-Diphenylbutane (N ₂)	meso-2,3-Diphenylbutane (N ₂)	meso-2,3-Diphenylbutane (N ₂)
--------------------------------------	---	---	---

3,4-Diphenylbutane (N ₂)	meso-3,4-Diphenylbutane (N ₂)	meso-3,4-Diphenylbutane (N ₂)	meso-3,4-Diphenylbutane (N ₂)
--------------------------------------	---	---	---

Table 36. Isomerization

Alkenyl Benzene	Reactants (Per cent by weight on aromatic + catalyst)	Catalyst	Contact Time (hours)	Temp. (°C)
1-Phenylpropene-1 (Propenylbenzene)	Dry caustic-alkali			heated
3-Phenylpropene-1 (Allylbenzene)	Charcoal		2-3 drops feed per 23.56 cc. cat. per min.	300
Allylbenzene	Ni on asbestos			360
Allylbenzene	Pd			300
Allylbenzene	Al ₂ O ₃			200-225
Allylbenzene	Cr ₂ O ₃		2-3 drops feed per 23.56 cc. cat. per min.	220
Allylbenzene	Fe ₂ O ₃		2-3 drops feed per 23.56 cc. cat. per min.	220
Allylbenzene	SiO ₂ gel		2-3 drops feed per 23.56 cc. cat. per min.	300
Allylbenzene	Clay		2-3 drops feed per 23.56 cc. cat. per min.	300
Allylbenzene	Infusorial earth			500
Allylbenzene	Infusorial-earth briquettes		(2 or 3 passes)	500
Allylbenzene	Dry caustic alkali			heated
Allylbenzene	KOH			b.p.
Allylbenzene	C ₂ H ₅ OH			130
Allylbenzene	KOH			
Allylbenzene	C ₂ H ₅ OH			
Allylbenzene	Propylbenzene (diluent)			
4-Phenylbutene-1	"Pyrex" glass tube		28 sec.	550
4-Phenylbutene-1	Pt, 30% Charcoal, 70%			300
4-Phenylbutene-1	Al ₂ O ₃		0.1 ml. feed per minute (1 pass)	225 or 250 or 300
4-Phenylbutene-1	Cr ₂ O ₃		0.1-0.15 ml. feed per minute	225 or 250
1-Phenylbutene-2	Alcoholic potash			b.p.
1-Phenylbutene-2	Alcoholic potash		(long)	160-180
5-Phenylpentene-1	Cr ₂ O ₃		0.1-0.15 ml. feed per minute	250
1-Phenyl-3-methylbutene-2	H ₂ SO ₄			b.p.
1-Phenyl-3-methylbutene-2	H ₃ PO ₄ , 85% H ₂ O, 15%			180
1-Phenyl-3-methylbutene-2	Alcoholic potash			
5-Phenylpentene-1	H ₂ SO ₄			
5-Phenylpentene-1	H ₂ SO ₄ , 90% H ₂ O, 10%	(74.3%)	40-50 min. at then 2 at	9-10 25-30

of Alkenyl Benzenes

Table 36. Isomerization of

Alkenyl Benzene	Reactants (Per cent by weight on aromatic + catalyst)	Catalyst	Contact Time (hours)	Temp. (°C.)
1-Phenylpentene-2	H ₂ SO ₄			
1-Phenylpentene-2	KOH	(25%)	1 day	150
	C ₂ H ₅ OH	(50%)		
6-Phenylhexene-1	H ₂ SO ₄ , 90%}		40-50 min.	at 9-10
6-Phenylhexene-1	H ₂ O, 10%}	(74.2%)	then 2	at 25-30
<i>o</i> -Allyltoluene	Al ₂ O ₃			220-225
<i>m</i> -Allyltoluene	Al ₂ O ₃			220-225
<i>p</i> -Allyltoluene	Al ₂ O ₃			220-225
<i>p</i> -Allyltoluene	Pt, 30%}			300
	Charcoal, 70%}			
<i>p</i> -Diallylbenzene	Al ₂ O ₃ (dehydrated at 360-400° C.)		2-3 drops feed per 31.4 cc. cat. per min.	300
1,1-Diphenylethylene	Infusorial-earth briquettes		(2 or 3 passes)	500
<i>cis</i> -1,2-Diphenylethylene (Isostilbene)	Sunlight			
Isostilbene	Sunlight			
Isostilbene	Sunlight		(long)	
Isostilbene			1	170-180
Isostilbene			1	170-178
Isostilbene				heated
Isostilbene				above 200
Isostilbene			distillation time	277-307
Isostilbene	"Pyrex" reaction vessel		91.7 min.	320
Isostilbene	"Pyrex" reaction vessel		200.3 min.	320
Isostilbene	"Pyrex" reaction vessel		23.4 min.	341
Isostilbene	"Pyrex" reaction vessel		62.7	341
Isostilbene	Ultraviolet light (90% be- ing 2537 Å.)		1	liquid-air temper- ature
	C ₂ H ₅ OH, 1.0 volume } (solvent)			
	Ether, 2.5 volumes }			
	Isopentane, 2.5 volumes }			
	Air absent			
Isostilbene (0.010 molar solution)	Ultraviolet light (90% be- ing 2537 Å.)		1 or 3	-90
	C ₂ H ₅ OH, 1 volume } (solvent)			
	Ether, 9 volumes }			
Isostilbene (0.00002 molar solution)	Ultraviolet light (2537 Å.)		0-4000 sec.	20
	"Iso-octane" (solvent)			
Isostilbene (0.005 molar solution)	Ultraviolet light (2537 Å.)		0-1	20
	"Iso-octane" (solvent)			
Isostilbene	Li		Li: 24	at room
	Ether (solvent)		Hg: "over-	at room
	Later, Hg and CO ₂		night"	
Isostilbene	Stilbene-dilithium		"instantly"	heat evolved
Isostilbene	Na		Na: 2 days	at room
	Ether (solvent)			
	Later, C ₂ H ₅ OH			
Isostilbene	Na		Na: 14 days	at room
	Ether (solvent)			
	Later, Hg			
Isostilbene	Stilbene-disodium		"instantly"	heat evolved

Alkenyl Benzenes—Continued

Pressure (atms.)	Products (Per cent by weight on original aromatic)				Reference
	Isomers		Other Products		
1 bomb	1-Methyltetralin				(73)
	1-Phenylpentene-1				(309)
1	1-Ethyltetralin				(73)
1	1-Ethyltetralin	(65%)			(471)
	<i>o</i> -Propenyltoluene				(338)
	<i>m</i> -Propenyltoluene				(338)
	<i>p</i> -Propenyltoluene				(338)
(CO ₂)	<i>p</i> -Propenyltoluene	(84%)	<i>p</i> -Allyltoluene	(16%)	(345)
(CO ₂)	<i>p</i> -Allylpropenylbenzene, 1 part	}			(342a)
	<i>p</i> -Dipropenylbenzene, 5 parts				
1	Stilbene				(456)
1	Stilbene				(428a)
1	Stilbene				(652)
1	Stilbene				(572)
	Stilbene				(567)
	Stilbene	(large %)			(572)
1	Stilbene				(570)
	Stilbene				(652)
1	Stilbene				(652)
sub-atm.	Stilbene	(82.8%)	Isostilbene	(17.2%)	(306)
sub-atm.	Stilbene	(83.0%)	Isostilbene	(17.0%)	(306)
sub-atm.	Stilbene	(81.7%)	Isostilbene	(19.3%)	(306)
sub-atm.	Stilbene	(82.2%)	Isostilbene	(17.8%)	(306)
1	Stilbene		Isostilbene		(350a)
1	Stilbene		Isostilbene		(350a)
1	Stilbene		Isostilbene		(350a)
1	Stilbene (29% of the excited molecules)		Isostilbene (unexcited molecules +68% of the excited molecules)		(350a)
1	Stilbene		Yellow substance (3% of the excited molecules)		(516)
1	Stilbene				(680)
1	Stilbene				(516)
1	Stilbene				(516)
1	Stilbene				(680)

Table 36. Isomerization of

Alkenyl Benzene	Reactants (Per cent by weight on aromatic + catalyst)	Catalyst	Contact Time (hours)	Temp. (°C.)
Isostilbene	O ₂		403 min.	214
Isostilbene	O ₂		23.3	214
Isostilbene	Br ₂	(trace)		
Isostilbene	Sunlight			
Isostilbene	Br ₂ and sunlight			
Isostilbene	CS ₂ (solvent)			
Isostilbene	Br ₂ and HBr in the dark			room
Isostilbene	C ₆ H ₆ (?)			
Isostilbene	I ₂	(trace)	(short)	
Isostilbene	Sunlight			
Isostilbene	I ₂	(trace)	(short)	
Isostilbene	Sunlight			
Isostilbene	BF ₃ and ether complex (b.p. 125°) in the dark		12	room
Isostilbene	BF ₃ and ether complex (b.p. 125°) in the dark		24	room
Isostilbene	BF ₃ and ether complex (b.p. 125°) in the dark		30	room
Isostilbene	BF ₃ and ether complex (b.p. 125°) in the dark		36	room
Isostilbene	BF ₃ and ether complex (b.p. 125°) in the dark		72	room
Isostilbene	BF ₃ and ether complex (b.p. 125°) in the dark		16	room
Isostilbene	BF ₃ in the dark		18	room
Isostilbene	CCl ₄ (solvent)			
Isostilbene	BF ₃ in the dark		19	room
Isostilbene	CCl ₄ (solvent)			
Isostilbene	BF ₃ in the dark			
Isostilbene	CCl ₄ (solvent)			
Isostilbene	HBr and O ₂ in the dark		few min.	room
Isostilbene	HBr and air in the dark		20–30 min.	room
(5% solution)	C ₆ H ₆ (solvent)			
Isostilbene	HBr and air in the dark		2	room
Isostilbene	C ₆ H ₆ (solvent)			
Isostilbene	HBr and air		1	room
Isostilbene	Diphenylamine			
Isostilbene	HBr and air		20	room
Isostilbene	Catechol			
Isostilbene	HBr and air in the light			room
Isostilbene	Ethyl mercaptan			
Isostilbene	C ₆ H ₆ (?)			
Isostilbene	HBr and air in the light			room
Isostilbene	Hydroquinone			
Isostilbene	C ₆ H ₆ (?)			
Isostilbene	HBr		over 20	room
Isostilbene	Reduced Cu			
Isostilbene	HBr		0.5–4	room
Isostilbene	Reduced Fe			
Isostilbene	HBr in the dark		0.5–3	room
Isostilbene	Reduced Ni			
Isostilbene	HBr in the dark		below 0.5	100
Isostilbene	Reduced Ni			
Isostilbene	HBr (0.015–0.08 <i>N</i>) in the dark		1–4 days	room
(5–10% solution)	Reduced Ni (0.1–0.5 g. per 4 cc. solution)			
Isostilbene	C ₆ H ₆ (solvent)			
Isostilbene	HBr	(large %)		room
Isostilbene	Reduced Ni			
Isostilbene	C ₆ H ₆ (?)			

Alkenyl Benzenes—*Continued*

Pressure (atms.)		Products		Refer- ences
		Isomers	(Per cent by weight on original aromatic) Other Products	
1 (O ₂)	Stilbene		(4.3%) An acid	(578)
1 (O ₂)	Stilbene		(12.8%) An acid	(578)
1	Stilbene			(652)
1	Stilbene			(567)
1	No Stilbene			(303)
1	Stilbene			(652)
1	Stilbene			(572)
1	Stilbene	(below 10%)		(447)
1	Stilbene	(38.1%)		(447)
1	Stilbene	(74.8%)		(447)
1	Stilbene	(92.3%)		(447)
1	Stilbene	(92.2%)		(447)
1	Stilbene	(81.0%)		(447)
1	Stilbene	(93.1%)		(447)
1	Stilbene	(93.1%)		(447)
1	Stilbene			(607)
1	Stilbene	(over 50%)		(608)
1	No stilbene			(303)
1	Stilbene	(20%)		(608)
1	No stilbene			(608)
1	No stilbene			(303)
1	No stilbene			(303)
1	Stilbene			(608)
1	Stilbene			(608)
1	Stilbene			(607)
1	Stilbene			(607)
1	No stilbene			(608)
1	Stilbene	(small %)		(608)

Table 36. Isomerization of

Alkenyl Benzene	Reactants	Contact Time (hours)	Temp. (°C.)
	Catalyst (Per cent by weight on aromatic + catalyst)		
Isostilbene	HBr Pd black	over 20	room
Isostilbene	HBr Pt black	over 20	room
Isostilbene	HBr Ascaridole	few min.- 30 min.	room
Isostilbene	C ₆ H ₆ (solvent) HBr in the dark	few min.	room
Isostilbene	Benzoyl peroxide HBr	few min.- 30 min.	room
Isostilbene	Benzoyl peroxide C ₆ H ₆ (solvent)	5-20 min.	room
Isostilbene	HBr in sunlight C ₆ H ₆ (solvent)	5-20 min.	room
Isostilbene	HBr in artificial light C ₆ H ₆ (solvent)	0.5-1.0 min.	room
Isostilbene	HBr in sunlight Air absent	1-4 days	room
Isostilbene	HBr in the dark	2	room
Isostilbene (5-10% solution)	HBr in the dark C ₆ H ₆ (solvent)		room
Isostilbene	HBr in the dark C ₆ H ₆ (solvent)		room
Isostilbene	Air absent HBr in the dark	0.5	100
Isostilbene	Air absent HBr in the dark	0.5	100
Isostilbene	Catechol (0.005 g. per 0.2 cc. isostilbene) Air absent	2	room
Isostilbene	HBr in the dark Catechol		room
Isostilbene	HBr in sunlight Catechol		room
Isostilbene	HBr in the dark Reduced Ni (0.020 g. per 0.2 cc. isostilbene)	40	room
Isostilbene	Catechol (0.005 g. per 0.2 cc. isostilbene) HBr in the light		room
Isostilbene	Hydroquinone C ₆ H ₆ (?)		room
Isostilbene	Air absent HBr in the dark	2	room
Isostilbene	Hydroquinone C ₆ H ₆ (solvent)		room
Isostilbene	HBr in the dark Thiophenol	2	room
Isostilbene	C ₆ H ₆ (solvent) HBr in the light		room
Isostilbene	Ethyl mercaptan C ₆ H ₆ (?)		room
Isostilbene	Air absent HBr in sunlight	1 min.	room
Isostilbene	Diphenylamine HBr in the dark		room
Isostilbene	Diphenylamine Diphenylamine in the dark		room
Isostilbene	HBr in the dark Reduced Ni		room
Isostilbene	Diphenylamine		room

References

Products				Products			
on original assembly	by weight on original assembly	Products	on original assembly	by weight on original assembly	Products	on original assembly	by weight on original assembly
(608)	(608)		(608)	(608)		(608)	(608)
Stillbene	1	Stillbene	1	Stillbene	1	Stillbene	1
(608)				(608)		(608)	
Stillbene	1	Stillbene	1	Stillbene	1	Stillbene	1
(303)				(303)		(303)	
Stillbene	1	Stillbene	1	Stillbene	1	Stillbene	1
(607)				(607)		(607)	
Stillbene	1	Stillbene	1	Stillbene	1	Stillbene	1
(303)				(303)		(303)	
Stillbene	1	Stillbene	1	Stillbene	1	Stillbene	1
(303)				(303)		(303)	
Stillbene	1	Stillbene	1	Stillbene	1	Stillbene	1
(303)				(303)		(303)	
Stillbene	1	Stillbene	1	Stillbene	1	Stillbene	1
(608)				(608)		(608)	
No stilbene	1	No stilbene	1	No stilbene	1	No stilbene	1
(608)				(608)		(608)	
No stilbene	1	No stilbene	1	No stilbene	1	No stilbene	1
(303)				(303)		(303)	
Stillbene	1	Stillbene	1	Stillbene	1	Stillbene	1
(608)				(608)		(608)	
No stilbene	1	No stilbene	1	No stilbene	1	No stilbene	1
(608)				(608)		(608)	
No stilbene	1	No stilbene	1	No stilbene	1	No stilbene	1
(303)				(303)		(303)	
Stillbene	1	Stillbene	1	Stillbene	1	Stillbene	1
(608)				(608)		(608)	
No stilbene	1	No stilbene	1	No stilbene	1	No stilbene	1
(608)				(608)		(608)	
No stilbene	1	No stilbene	1	No stilbene	1	No stilbene	1
(303)				(303)		(303)	
Stillbene	1	Stillbene	1	Stillbene	1	Stillbene	1
(608)				(608)		(608)	
No stilbene	1	No stilbene	1	No stilbene	1	No stilbene	1
(608)				(608)		(608)	
No stilbene	1	No stilbene	1	No stilbene	1	No stilbene	1
(303)				(303)		(303)	

Table 36. Isomerization of

Alkenyl Benzene	Reactants	Catalyst (Per cent by weight on aromatic + catalyst)	Contact Time (hours)	Temp. (°C.)
Isostilbene	HCl		4	190
Isostilbene	HCl, 20% H ₂ O, 80%			b.p.
Isostilbene	HCl Ascaridole C ₆ H ₆ (solvent) (In the light or dark)			room
Isostilbene	HCl Benzoyl peroxide C ₆ H ₆ (solvent) (In the light or dark)			room
Isostilbene	HCl Catechol C ₆ H ₆ (solvent) (In the light or dark)			room
Isostilbene	HCl Hydroquinone C ₆ H ₆ (solvent) (In the light or dark)			room
Isostilbene	HCl Thiophenol C ₆ H ₆ (solvent) (In the light or dark)			room
Isostilbene	HNO ₃ (fuming)		several min.	
Isostilbene	HNO ₃ (fuming)		0.5	room
Isostilbene	HNO ₃ (fuming)			
Isostilbene	C ₆ H ₅ . CO ₂ H		400 min.	214
Isostilbene	C ₆ H ₅ . CO ₂ H		3400 min.	214
Isostilbene	C ₆ H ₅ . CO ₂ H		400 min.	223
Isostilbene	C ₆ H ₅ . CO ₂ H		20	223
Isostilbene	C ₆ H ₅ . CO ₂ H			200
<i>trans</i> -1,2-Diphenylethylene (Stilbene)	"Pyrex" reaction vessel		16.6 min.	320
Stilbene	"Pyrex" reaction vessel		33.0 min.	320
Stilbene	"Pyrex" reaction vessel		61.0 min.	320
Stilbene	"Pyrex" reaction vessel		10.8 min.	341
Stilbene	"Pyrex" reaction vessel		27.3 min.	341
Stilbene	Ultraviolet light (3130 Å.) C ₆ H ₁₄ (solvent)		10-60 min.	room
Stilbene	Ultraviolet light (2537 Å.) "Iso-octane" (solvent)			20
Stilbene	Ultraviolet light C ₆ H ₆ (solvent)			room
Stilbene	Ultraviolet light C ₆ H ₆ (solvent)		8 days	
Stilbene	C ₆ H ₅ . CO ₂ H			200
<i>o</i> -Phenyl-1,1-diphenylethylene	PCl ₅			
1,1,3-Triphenylpropene-1	H ₂ SO ₄ (94.8%)		8 days	room

Alkenyl Benzenes—Continued

Pressure (atms.)	Products				Refer- ences
	(Per cent by weight on original aromatic)				
	Isomers	Other Products			
1 (N ₂)	Stilbene			(578)	
1	Stilbene			(570)	
1	No stilbene			(303)	
1	No stilbene			(303)	
1	No stilbene			(303)	
1	No Stilbene			(303)	
1	No stilbene			(303)	
1	Stilbene			(567)	
1	Stilbene	(large %)		(572)	
1	Stilbene	(2.8%)		(300)	
1 (N ₂)	Stilbene	(16.8%)	Decomposition products	(578)	
1 (N ₂)	Stilbene	(5.65%)		(578)	
1 (N ₂)	Stilbene	(13.7%)		(578)	
1 (N ₂)	Stilbene	(96%)	Isostilbene	(4%) (578)	
1 (N ₂)	Isostilbene	(4.3%)	Stilbene	(95.7%) (306)	
sub-atm.	Isostilbene	(6.0%)	Stilbene	(94.0%) (306)	
sub-atm.	Isostilbene	(6.0%)	Stilbene	(94.0%) (306)	
sub-atm.	Isostilbene	(6.3%)	Stilbene	(93.7%) (306)	
sub-atm.	Isostilbene	(7.6%)	Stilbene	(92.4%) (306)	
1	Isostilbene		Stilbene	(556)	
1	Isostilbene (35% of the excited molecules)		Stilbene (unexcited mole- cules+the 17% of ex- cited molecules that do not fluoresce+the 48% of excited molecules that do fluoresce)	(350a)	
1	Isostilbene		Stilbene	(350a)	
1	Isostilbene	(9.0%)		(567)	
1 (N ₂)	Isostilbene	(4.0%)	Stilbene	(96.0%) (578)	
	9-Phenyl-9,10-dihydro- phenanthrene			(50)	
1	1,3-Diphenylindane	(16%)	1,1,3-Triphenylpropene-1	(517)	

Table 36. Isomerization of

Alkenyl Benzene	Reactants (Per cent by weight on aromatic + catalyst)	Catalyst	Contact Time (hours)	Temp. (°C.)
1,1,3-Triphenylpropene-1	Li Ether (solvent) Later, diphenylbromo- methane (9.2 grams per 10 grams of 1,1,3-tri- phenylpropene-1)			room
1,2,3-Triphenylpropene	Unstated (work of Ra- mart and Amagat re- ferred to)		unstated	unstated
1,1,3,3-Tetraphenylpropene	Li (3%) Ether (solvent) (92%) Later, C ₂ H ₅ OH		8 days to dissolve Li	room
1,2,3,3-Tetraphenylpropene-1	Na and (? ether) Later, Hg		reacts slowly with Na	room
1,1,3,3,3-Pentaphenylpropene	H ₂ SO ₄ (3.8%) CH ₃ · CO ₂ H (91.7%) H ₂ SO ₄ (trace)		3	b.p.
1,3-Diphenylbutene-1			3-4 years	room
1,3-Diphenylbutene-1	H ₂ SO ₄ , 50% H ₂ O, 50% H ₂ SO ₄ -treated pumice	(93.5%)	40	b.p.
2,3-Diphenylbutene-2 (m.p. 104°, β-form)			"several minutes"	heated
1,1,3,3-Tetraphenylbutene	I ₂	(9.09%)	over 6	100
1,1,3,3-Tetraphenylbutene	Li Ether (solvent) Later, C ₂ H ₅ OH		6 days to dissolve Li	room
1,1,3,3-Tetraphenylbutene	"Floridin"		6 days	215
1,1,3,3-Tetraphenylbutene	SnCl ₄ (4.7%) C ₆ H ₆ (solvent) (83.4%)		1 week	room
1,1,3,3-Tetraphenylbutene	SnCl ₄ (4.7%) HCl (gas) C ₆ H ₆ (solvent) (83.4%)		1 week	room
1,1,3,3-Tetraphenylbutene	SnCl ₄ (50 cc. per 5 g. of the butene)		1 week	b.p.
1,1,3,3-Tetraphenylbutene	H ₂ SO ₄		(long)	room
1,1,3,3-Tetraphenylbutene	Dimethyl sulfate	(26.5%)	6	100
1,2,3,4-Tetraphenylbutene-1 (m.p. 96°)	Na Ether (solvent) Later, C ₂ H ₅ OH			room
1,2,3,4-Tetraphenylbutene-1 (m.p. 150°)	Na Ether (solvent) Later, C ₂ H ₅ OH (?)		Na: 3 days	room
1,2,3,4-Tetraphenylbutene-1 (m.p. 150°)	Na (5.5%) Amyl alcohol (86%)			b.p.
1,2,3,4-Tetraphenylbutene-1 (m.p. 150°)	Benzene (solvent) (82.5%) HCl (to saturation) SnCl ₄ (14.3%) After 7 days, ice-cold fum- ing hydrochloric acid		7 days	room
1,2,3,4-Tetraphenylbutene-1 (m.p. 150°)	Red phosphorus (4.0%) HI soln. (d. = 1.7) (15.2%) CH ₃ · CO ₂ H (78.5%)		4	b.p.
1,2,3,4-Tetraphenylbutene-2 (m.p. 80°)				distilla- tion temp.

Alkenyl Benzenes—Continued

Pressure (atms.)	Products (Per cent by weight on original aromatic)			References
	Isomers	Other Products		
1	1,3-Diphenylindane	(10%) 1,1,2,2-Tetraphenylethane (large %)		(518)
	1,2-Diphenylindane			(52)
1	1,2,3-Triphenylindane			(516)
1	1,1,2,3-Tetraphenyl- propene-1	1,1,2,3,4,5,6,6-Octaphenyl- hexadiene-1,5		(53)
1	1,1,3,3-Tetraphenylindane			(316)
1	1-Methyl-3-phenylin- dane (?)	1,3-Diphenylbutene-1	(trace)	(569)
1	1-Methyl-3-phenylin- dane	Polymers	(20%)	(468)
1	2,3-Diphenylbutene-2 (m.p. 65°, α -form)	2,3-Diphenylbutene-2 (m.p. 104°, β -form)	(over 27.5%)	(458)
1	1-Methyl-1,3,3-tri- phenylindane (?)			(54)
1	1,1,4,4-Tetraphenyl- butene-2	1,1-Diphenylethane		(55)
	1-Methyl-1,2,3-tri- phenylindane	1,1-Diphenylethylene		
	1-Methyl-1,3,3-triphenylindane	1,1,4,4-Tetraphenylbutadiene-1,3		(332)
bomb	No isomers	1,1,3,3-Tetraphenylbutene	(80%)	(522)
1		1,1-Diphenylethylene	(14%)	(522)
1	1-Methyl-1,3,3-tri- phenylindane			(90%)
1	1-Methyl-1,3,3-tri- phenylindane			(90%)
1	1-Methyl-1,3,3-tri- phenylindane			(88.9%)
1	1,2,3,4-Tetraphenyl- butene-2 (m.p. 80°)			
1	1-Benzyl-2,3-diphenylin- dane			
1	1,2,3,4-Tetraphenylbutene-2 (m.p. 80°)		(small %)	
1	1-Benzyl-2,3-diphenylin- dane	1,2,3,4-Tetraphenyl- butane	(30%)	
1	1-Benzyl-2,3-diphenylindane			
1	1-Benzyl-2,3-diphenylindane			
high vacuum	1-Benzyl-2,3-diphenylindane			

Table 36. Isomerization of

Reactants	Catalyst	Contact Time	Temp.
(Per cent by weight on aromatic + catalyst)		(hours)	(°C.)
Alkenyl Benzene			
1,2,3,4-Tetraphenylbutene-2 (m.p. 80°)	Na Ether (solvent) Later, C ₂ H ₅ OH	Na: 1 week	room
2,4-Diphenyl-4-methyl- pentene-2	AlCl ₃ ("equimolar" with the diphenylmethyl- pentene) Benzene (solvent)	2 days	room
2,4-Diphenyl-4-methyl- pentene-2	SnCl ₄ (9.09%)	20	room

Table 37. Isomerization

Reactants	Catalyst	Contact Time	Temp.
(Per cent by weight on aromatic + catalyst)		(hours)	(°C.)
Alkadienyl Benzene			
Phenylpropadiene	Alcoholic potash	6.5	105-110
Tetraphenylpropadiene	I ₂ (0.7%) Benzene (solvent) (92.3%)	12	room
Tetraphenylpropadiene	I ₂ (0.7%) Benzene (solvent) (92.3%)		heated
Tetraphenylpropadiene	HBr (gas)	(long)	room
Tetraphenylpropadiene	HBr (gas)		room
Tetraphenylpropadiene	CH ₃ · CO ₂ H HCl (gas)	(long)	room
Tetraphenylpropadiene	20% HCl (aqueous) (90.9%)		b.p.
Tetraphenylpropadiene	HCl (gas) CH ₃ · CO ₂ H (solvent)	several	room
Tetraphenylpropadiene	HCl (gas) CH ₃ · CO ₂ H (solvent)	5 min.	b.p.
Tetraphenylpropadiene	CH ₃ · CO ₂ H	8	b.p.
Triphenyl-(1-naphthyl)- propadiene	HCl (gas) CH ₃ · CO ₂ H (solvent)		b.p.
Triphenyl-(1-naphthyl)- propadiene	<i>p</i> -Toluenesulfonic acid Benzene (solvent)		b.p.
1,3-Diphenyl-1- <i>p</i> -tolyl-3- (1-naphthyl)propadiene	HCl (gas) CH ₃ · CO ₂ H (solvent)		b.p. (?)
<i>d</i> -1,3-Diphenyl-1,3-di-(1- naphthyl)propadiene	Decalin (solvent) (95%)	48	190
<i>d</i> -1,3-Diphenyl-1,3-di-(1- naphthyl)propadiene	Decalin (solvent)	9.5	b.p.
<i>dl</i> -1,3-Diphenyl-1,3-di-(1- naphthyl)propadiene	I ₂ (0.7%) Benzene (solvent) (92.3%)	1	100
<i>dl</i> -1,3-Diphenyl-1,3-di-(1- naphthyl)propadiene	HCl (gas) CH ₃ · CO ₂ H (solvent) (99.9%)	5 min.	b.p.
1,1,3-Triphenylbutadiene- 1,2	H ₂ SO ₄ (5%) CH ₃ · CO ₂ H (solvent) (87%)	0.25	heated (?)
1,1,3-Triphenylbutadiene- 1,2	CH ₃ · CO ₂ H (90%)	4	b.p.
1,1,3-Triphenylbutadiene- 1,2	Acetic anhydride (90%)	4	b.p.
1-Phenylbutadiene-1,3	"Floridin"	0.05 g. feed per minute	290-300

Alkenyl Benzenes—Continued

Pressure (atms.)	Products		Refer- ences
	Isomers (Per cent by weight on original aromatic)	Other Products	
1	1-Benzyl-2,3-diphenylin- dane (30%)	1,2,3,4-Tetraphenyl- butane	(57)
1	1,1,3-Trimethyl-3- phenylindane (20%)	Resins	(51)
1	1,1,3-Trimethyl-3- phenylindane (40%)		(51)

of Alkadienyl Benzenes

Pressure (atms.)	Products		Refer- ences
	Isomers (Per cent by weight on original aromatic)	Other Products	
1	1-Phenylpropyne-1		(214)
1	1,1,3-Triphenylindene	I ₂ (10%)	(613)
1	1,1,3-Triphenylindene	I ₂ (10%)	(613)
1	1,1,3-Triphenylindene	Addition product	(613)
1	1,1,3-Triphenylindene		(613)
1	1,1,3-Triphenylindene	Addition product	(613)
1	1,1,3-Triphenylindene		(613)
1	1,1,3-Triphenylindene		(613)
1	1,1,3-Triphenylindene		(317)
1	1,1,3-Triphenylindene		(613)
1	1,3,3-Triphenyl-3- α - naphthindene		(106)
1	1,3,3-Triphenyl-3- α - naphthindene		(106)
	1,3-Diphenyl-3- <i>p</i> -tolyl-3- α -naphthindene		(106)
sealed tube	<i>dl</i> -1,3-Diphenyl-1,3-di- (1-naphthyl)propa- diene (40%)		(358)
1	<i>dl</i> -1,3-Diphenyl-1,3-di- (1-naphthyl)propa- diene (small %)		(358)
1	1,3-Diphenyl-3-(1- naphthyl)-3- α -naphthin- dene	I ₂	(358)
1	1,3-Diphenyl-3-(1- naphthyl)-3- α -naphthin- dene		(358)
1	1-Methyl-1,3-diphenylindene (?)		(679)
	1,1-Diphenyl-3-methylindene (?)		
1	1,1,3-Triphenylbutadiene-1,3 (?)		(679)
1	1,1,3-Triphenylbutadiene-1,3 (?)		(679)
1	4-Phenylbutyne-1 (?)	Polymers (65-70%)	(555)

Table 37. Isomerization of

Reactants	Catalyst	Contact Time	Temp.
Alkadienyl Benzene	(Per cent by weight on aromatic + catalyst)	(hours)	(°C.)
<i>cis</i> -1-Phenylbutadiene-1,3	CaCl ₂ wetted with dilute hydrochloric acid	"Overnight" then (time of distillation) 2 months	at room at 76
<i>cis-cis</i> -1,4-Diphenylbutadiene-1,3	Sunlight		
<i>cis-cis</i> -1,4-Diphenylbutadiene-1,3	Sunlight CH ₃ . CO ₂ H	17 days	
<i>cis-trans</i> -1,4-Diphenylbutadiene-1,3	Sunlight	0.25	
1,1,2,3-Tetraphenylbutadiene-1,3	CH ₃ . CO ₂ H H ₂ SO ₄ ("a drop")	5 min.	b.p.
1,2,3,4-Tetraphenylbutadiene-1,3	Na Ether (solvent) Later, Hg for demetalation	Na: 3 days Hg: 1 day	room
1,2,3,4-Tetraphenylbutadiene-1,3	SnCl ₄ Benzene		room
	(19%) (73%)		

Table 38. Isomerization

Reactants	Catalyst	Contact Time	Temp.
Alkapolyenyl Benzene	(Per cent by weight on aromatic + catalyst)	(hours)	(°C.)
<i>cis</i> -1,4-Diphenylbutatriene	Sunlight		
<i>cis</i> -1,4-Diphenylbutatriene	Sunlight	14 days	
<i>cis</i> -1,4-Diphenylbutatriene	I ₂ (trace) and sunlight	(long)	
1,1,5,5-Tetraphenyl-3-styrylpentadiene-1,4	Phenyl-lithium Ether (solvent) Later, CH ₃ OH in excess	2 days with C ₆ H ₅ Li	room
1,1,6,6-Tetraphenyl-3,4-di- <i>tert</i> -butylhexatetraene-1,2,4,5	40%-Sodium amalgam Ether (solvent) Later, 10% solution of tetraphenylethylene dibromide	36	room
1,1,6,6-Tetraphenyl-3,4-di- <i>tert</i> -butylhexatetraene-1,2,4,5	Sodium amalgam Ether (solvent) Later, solution of tetraphenylethylene dibromide		
1,1,6,6-Tetraphenyl-3,4-di- <i>tert</i> -butylhexatetraene-1,2,4,5	HCl (gas) CH ₃ . CO ₂ H	48	b.p.
1,1,6,6-Tetraphenyl-3,4-di- <i>tert</i> -butylhexatetraene-1,2,4,5			heated (?)
1,1,6,6-Tetraphenyl-3,4-di- <i>tert</i> -butylhexatetraene-1,2,4,5	H ₂ SO ₄ CH ₃ . CO ₂ H	several	heated
	(3.2%) (92.6%)		
<i>yellow</i> -1,8-Diphenyloctatet- <i>rene</i> -1,3,5,7	Sunlight	3 months	
<i>yellow</i> -1,8-Diphenyloctatet- <i>rene</i> -1,3,5,7	I ₂ and sunlight CHCl ₃ (solvent)	several days	

Alkadienyl Benzenes—Continued

Pressure (atms.)	Products		Refer- ences
	Isomers	Other Products	
1	<i>trans</i> -1-Phenylbutadiene-1,3 (100%)		(395)
11 mm. Hg			
1	<i>trans-trans</i> -1,4-Diphenyl- butadiene-1,3		(572)
1	<i>trans-trans</i> -1,4-Diphenyl- butadiene-1,3 (33.3%)		(572)
1	<i>trans-trans</i> -1,4-Diphenyl- butadiene-1,3		(572)
1	1-Methyl-1,2,3-tri- phenylindene (100%)		(316a)
1	1-Benzylidene-2,3-di- phenylindane (about 67% on the "product")	1-Benzyl-2,3-diphenylin- dane (about 33% on the "product")	(57)
1	1-Benzyl-2,3-diphenylin- dene (60%)	1,2,3,4-Tetraphenylbutane	(57)

cf Alkapolyenyl Benzenes

Pressure (atms.)	Products		Refer- ences
	Isomers	Other Products	
1	<i>trans</i> -1,4-Diphenylbutatriene		(229)
1	<i>trans</i> -1,4-Diphenylbutatriene		(572)
1	<i>trans</i> -1,4-Diphenylbutatriene		(572)
1 (N ₂)	1,1,5,5-Tetraphenyl-3-phenethyl- idene-pentadiene-1,4		(654)
1 (N ₂)	Isomer "B," m.p. 179.3– 180.3° (25.5%)		(3)
	Isomer "B," m.p. 179–180°		(175)
1	Isomer "A," m.p. 173– 174° (60%)		(3)
1	Isomer "A," m.p. 176° (i.e., 1,1'-Di- <i>tert</i> -butyl- 3,3'-diphenyl-1,1'- biindene)		(175)
1	Isomer "A"		(3)
1 (CO ₂)	<i>white</i> -1,8-Diphenyloctate- trene-1,3,5,7		(566)
1 (CO ₂)	<i>white</i> -1,8-Diphenyloctate- trene-1,3,5,7	Resin	(566)

Table 39. Isomerization

Alkynyl Benzene	Reactants (Per cent by weight on alkynyl benzene + catalyst)	Catalyst	Contact Time (hours)	Temp. (°C.)
1-Phenylpropyne-1	NaNH ₂		2	110
4-Phenylbutyne-1	Cr ₂ O ₃		0.1 ml. feed per minute	250
4-Phenylbutyne-1	"Floridin"		0.05 g. feed per minute	250
1,1,4,4-Tetraphenylbutyne-2	NaOH			
1,1,4,4-Tetraphenylbutyne-2	C ₂ H ₅ OH			
	C ₂ H ₅ ONa (9.5%)		1	100
	C ₂ H ₅ OH (solvent) (88.9%)			
1,1,4,4-Tetra- <i>p</i> -tolylbutyne-2	C ₂ H ₅ ONa (9.0%)		3	b.p.
	C ₂ H ₅ OH (solvent) (89.5%)			
1,1-Diphenyl-4,1-dimethylpentyne-2 (or Na derivative)	H ₂ O			
1,3,3,4,4,6-Hexaphenylhexadiyne-1,5	Petroleum ether (solvent)		1	room
Isomer (m.p. 179°) related to 1,3,3,4,4,6-Hexaphenylhexadiyne-1,5				m.p.
Isomer (m.p. 172–173°) related to 1,3,3,4,4,6-Hexaphenylhexadiyne-1,5	HCl		4	b.p.
	CH ₃ . CO ₂ H (solvent)			
Isomer (m.p. 179°) related to 1,3,3,4,4,6-Hexaphenylhexadiyne-1,5	Xylene (solvent) and any one of the following substances: K ₃ Fe(CN) ₆ HgO PbO Pb ₃ O ₄ K ₂ S ₂ O ₈			heated
2,2,9,9-Tetramethyl-5,5,6,6-tetraphenyldecadiyne-3,7				slowly melted
2,2,9,9-Tetramethyl-5,5,6,6-tetraphenyldecadiyne-3,7	Hexane (solvent) (96%) Air present		3–250 min.	27.5
2,2,9,9-Tetramethyl-5,5,6,6-tetraphenyldecadiyne-3,7	Heptane (solvent) (98%)		1	b.p.
2,2,9,9-Tetramethyl-5,5,6,6-tetraphenyldecadiyne-3,7	Ether (solvent)		12	room
2,2,9,9-Tetramethyl-5,5,6,6-tetraphenyldecadiyne-3,7	Ether (solvent)		2 days	room
2,2,9,9-Tetramethyl-5,5,6,6-tetraphenyldecadiyne-3,7	Ether (solvent)		5 days	room
2,2,9,9-Tetramethyl-5,5,6,6-tetraphenyldecadiyne-3,7	Ether (solvent)		few min.	50
2,2,9,9-Tetramethyl-5,5,6,6-tetraphenyldecadiyne-3,7	Acetone (solvent) (99%)		0.75	b.p.

Table 39. Isomerization of

Alkynyl Benzene	Reactants (Per cent by weight on alkynyl benzene + catalyst)	Catalyst	Contact Time (hours)	Temp. (°C.)
2,2,9,9-Tetramethyl-5,5,6,6-tetraphenyldecadiyne-3,7	1% Sodium amalgam Ether (solvent) Later, C ₂ H ₅ OH		40	room
2,2,9,9-Tetramethyl-5,5,6,6-tetraphenyldecadiyne-3,7	1% Sodium amalgam Ether (solvent) Later, C ₂ H ₅ OH		5 days	room
2,2,9,9-Tetramethyl-5,5,6,6-tetraphenyldecadiyne-3,7	1% Sodium amalgam Ether (solvent) Later, C ₂ H ₅ OH		8 days	room
2,2,9,9-Tetramethyl-5,5,6,6-tetra-biphenyldecadiyne-3,7	Toluene (solvent)		10	room
3,10-Dimethyl-3,10-diethyl-6,6,7,7-tetraphenyldodecadiyne-4,8			(short)	0
3,10-Dimethyl-3,10-diethyl-6,6,7,7-tetraphenyldodecadiyne-4,8	Ether (solvent)		(long)	room

Table 40. Isomerization of Condensed Aromatics (Indanes, Indenes,

Condensed Aromatic	Reactants (Per cent by weight on aromatic + catalyst)	Catalyst	Contact Time (hours)	Temp. (°C.)
1-(1,5-Dimethyl-4-hexenylidene)indene	H . CO ₂ H	(79.1%)	12	140
3-Phenylindene	Pumice			dark-red heat
3- <i>p</i> -Tolylindene	Pumice			dark-red heat
1-Benzylindene	KOH CH ₃ OH (solvent)			
1-Benzylindene	CH ₃ OK CH ₃ OH (solvent)		12	room
1-Diphenylmethylene-indane	Conc. hydrochloric acid		1	heated
1-Benzhydrylindene	KOH CH ₃ OH (solvent)			
1-Benzhydrylindene	CH ₃ OK CH ₃ OH (solvent)		24	room
1,2-Diphenylindene	KOH			
1,2-Diphenylindene	KOH C ₂ H ₅ OH (solvent)			b.p.
1,2-Diphenylindene	KOH C ₂ H ₅ OH (solvent)	(0.6%) (89%)		b.p.
1,3-Dibenzylidene-indane (?)			(long)	over 213
1,3-Dibenzylidene-indane (?)			time of distillation	250-260
1-Benzhydryl-3- <i>sec</i> -butylindene (?) of m.p. 121-123°	CH ₃ OK CH ₃ OH (solvent)		0.5-1.0	b.p.

Alkynyl Benzenes—Continued

Pressure (atms.)	Products		Refer- ences
	(Per cent by weight on original alkynyl benzene) Isomers	Other Products	
1 (N ₂)	1,1,6,6-Tetraphenyl-3,4- di- <i>tert</i> -butylhexa- tetrene-1,2,4,5 (?) + (?) Isomer "B" of m.p. 181° (70% total)		(564)
1 (N ₂)	1,1,6,6-Tetraphenyl-3,4- di- <i>tert</i> -butylhexa- tetrene-1,2,4,5 (?) + (?) Isomer "B" of m.p. 181°		(564)
1 (N ₂)	1,1,6,6-Tetraphenyl-3,4- di- <i>tert</i> -butylhexa- tetrene-1,2,4,5 (?) + (?) Isomer "B" of m.p. 181°		(564)
1	Isomer (m.p. 166°)		(592)
1	Isomer (m.p. 108°)		(242)
sub-atm.	Isomer (m.p. 106.5–108°) (50%)		(242)

Fluorenes, Naphthalenes, Anthracenes, Phenanthrenes, Naphthacenes)

Pressure (atms.)	Products		Refer- ences
	(Per cent by weight on original condensed aromatic) Isomers	Other Products	
	1-Isopropyl-4-methyl-2,3- dihydrofluorene (?)		(491)
16 mm. Hg (CO ₂)	2-Phenylindene (33%)		(88)
16 mm. Hg (CO ₂)	2- <i>p</i> -Tolylindene (16.5%)		(88)
	3-Benzylindene		(127)
1	3-Benzylindene		(126)
1	3-Benzhydrylindene		(126)
	3-Benzhydrylindene		(127)
1	3-Benzhydrylindene		(126)
1	2,3-Diphenylindene		(230)
	2,3-Diphenylindene		(428)
1	2,3-Diphenylindene		(69)
1	1-Benzylidene-3-benzyl- indene		(579)
12 mm. Hg	1-Benzylidene-3-benzyl- indene		(579)
1	1- <i>sec</i> -Butyl-3-benzhydryl- indene (?) of m.p. 94–95°		(656)

Table 40. Isomerization of Condensed Aromatics (Indanes, Indenes,

Condensed Aromatic	Reactants (Per cent by weight on aromatic + catalyst)	Catalyst	Contact Time (hours)	Temp. (°C.)
1-Benzylidene-3- <i>p</i> -methylbenzylindene	KOH CH ₃ OH (solvent)			b.p.
1- <i>p</i> -Methylbenzylidene-3-benzylindene	KOH CH ₃ OH (solvent)			b.p.
1- <i>p</i> -Isopropylbenzylidene-3-benzylindene	CH ₃ OK CH ₃ OH (solvent)		10	b.p.
1-Benzylidene-3-benzhydrylindene 1,1,3-Triphenylindene	CH ₃ OK CH ₃ OH (solvent) Na		1	b.p.
1-Methyl-1,3,3-triphenylindane	"Floridin"		6 days	215
1-Biphenylene-3-phenylindene	40%-Sodium amalgam (an excess) Ether (solvent) Alcohol (for demetalation)		2 days for metalation	room
1-Biphenylene-3-phenylindene	Li (an excess) Ether (solvent)		3 days	
1,2-Diphenyl-3- <i>p</i> -tolylindene	40%-Sodium amalgam (an excess) Ether (solvent)		3	room
1,2-Diphenyl-3- <i>p</i> -tolylindene	Alcoholic potash (5% solution) (used 15 cc. per 0.5 g. aromatic)		1.25	b.p.
1- <i>p</i> -Tolyl-2,3-diphenylindene	40%-Sodium amalgam (an excess) Ether (solvent)		3	room
1-Biphenylene-4-phenylbutene-2	Na (4.3%) C ₂ H ₅ OH (84.9%)		2	b.p.
1-Biphenylene-4-phenylbutene-2	Piperidine C ₂ H ₅ OH (solvent)		(long)	b.p.
1-Biphenylene-2,3-diphenylbutadiene-1,3	CH ₃ . CO ₂ H (96%?) H ₂ SO ₄ (1%?)		1	b.p.
1,4-Dihydronaphthalene	C ₂ H ₅ ONa (10% solution)			100-105
1,4-Dihydronaphthalene	C ₂ H ₅ ONa (5% solution)			140-150
1,4-Dihydronaphthalene	C ₂ H ₅ ONa (approx. 10% solution)		3-4	150
1-Methylnaphthalene	Silica gel			420
1-Ethylnaphthalene	Silica gel			420-430
1-Methylene-2-methyl-1,4-dihydronaphthalene	HCl CH ₃ . CO ₂ H } (78.5%)		4	b.p.
1,6-Dimethylnaphthalene	Silica gel			400-420
1-Allylnaphthalene	Activated Al ₂ O ₃			500-550
1-Allylnaphthalene	Al ₂ O ₃		(long)	300
1-Allylnaphthalene	KOH C ₂ H ₅ OH			b.p.
1-Isopropenyl-1,2,3,4-tetrahydronaphthalene	C ₂ H ₅ ONa C ₂ H ₅ OH (solvent)		8	140-150
1-Phenylnaphthalene	Silica gel Cobalt silicate			350

Fluorenes, Naphthalenes, Anthracenes, Phenanthrenes, Naphthacenes)—*Continued*

Pressure (atms.)	Products (Per cent by weight on original condensed aromatic)		Refer- ences
	Isomers	Other Products	
1	Equilibrium mixture of m.p. 70° containing 1-benzylidene-3- <i>p</i> - methylbenzyl-indene and 1- <i>p</i> - methylbenzylidene-3-benzyl- indene		(59)
1	Equilibrium mixture of m.p. 70° containing 1-benzylidene-3- <i>p</i> - methylbenzyl-indene and 1- <i>p</i> - methylbenzylidene-3-benzyl- indene		(59)
1	"Equilibrium mixture" of m.p. 71–73° containing 1-benzyl- dene-3- <i>p</i> -isopropylbenzyl- indene and 1- <i>p</i> -isopropyl- benzylidene-3-benzylindene		(59)
1	1-Diphenylmethylene-3- benzylindene		(656)
1	1,2,3-Triphenylindene (Na derivative)		(678)
bomb	No isomers	1-Methyl-1,3,3-triphenyl- indane (100%)	(332)
1 (N ₂)	1,2,3,4-Dibenzo-9-phenyl- fluorene (Na derivative)		(313) (314)
1	1,2,3,4-Dibenzo-9-phenyl- fluorene (83%)		(316)
sealed tube	1- <i>p</i> -Tolyl-2,3-diphenylindene 1,2-Diphenyl-3- <i>p</i> -tolylindene (equilibrium mixture) = 1.083		(315)
1	1- <i>p</i> -Tolyl-2,3-diphenylindene 1,2-Diphenyl-3- <i>p</i> -tolylindene (equilibrium mixture) = 9		(315)
sealed tube	1- <i>p</i> -Tolyl-2,3-diphenylindene 1,2-Diphenyl-3- <i>p</i> -tolylindene (equilibrium mixture) = 1.273		(315)
1	Isomer (m.p. 81–82°) (approximately 88%)		(580)
1	Isomer (m.p. 81–82°)	1-Biphenylene-4-phenyl- butene-2	(580)
1	1-Biphenylene-2-phenyl-3- methylindene (75%)		(316a)
	1,2-Dihydronaphthalene		(573)
	1,2-Dihydronaphthalene		(574)
	1,2-Dihydronaphthalene ("100%")		(530)
(N ₂)	2-Methylnaphthalene (39%)		(365)
(N ₂)	2-Ethylnaphthalene		(365)
1	1,2-Dimethylnaphthalene (58.2%)		(529)
15 mm. Hg (CO ₂)	2,6-Dimethylnaphthalene (20%)	1,6-Dimethylnaphthalene	(365)
1	1-Propenylnaphthalene		(185)
	1-Propenylnaphthalene		(342a)
	1-Propenylnaphthalene		(585)
sealed tube	1-Isopropylidene-1,2,3,4- tetrahydronaphthalene (75%)		(299)
(air or H ₂)	2-Phenylnaphthalene		(365)

Table 40. Isomerization of Condensed Aromatics (Indanes, Indenes,

Condensed Aromatic	Reactants (Per cent by weight on aromatic + catalyst)	Catalyst	Contact Time (hours)	Temp. (°C.)
1-Phenylnaphthalene (<i>Cont.</i>)	Copper silicate (used individually)			
1-Benzyl-naphthalene				"glowing"
1-Benzyl-naphthalene	Pumice		7-10 portions of 2-3 g. feed	"glowing"
1,1'-Dinaphthyl	AlCl ₃ (11%) CS ₂ (87%)			b.p.
1,2,3-Triphenylnaphthalene	Li Ether (solvent) C ₂ H ₅ OH (for demetalation)		8 days for me- tallation	room
1,2,3,4,4a,9,9a,10-Octa- hydroanthracene	MoS ₂ (4.76%)		2 at then	340-350
1,2,3,4,5,6,7,8-Octa- hydroanthracene	MoS ₂ (4.76%)		1.5 at 2	360-370 335
1,2,3,4,5,6,7,8-Octa- hydroanthracene	MoS ₂ (4.76%)		2.4	390
1,2,3,4,5,6,7,8-Octa- hydroanthracene	AlCl ₃ (4.76%)		3	70-80
9-Benzohydrylidene-10- phenyl-9,10-dihydro- anthracene	Na Ether (solvent) C ₂ H ₅ OH (for demetalation)		10 weeks for re- placement of H by one Na	room
1,4,9,10-Tetraphenylanthracene	H . CO ₂ H (90.9%)		3	b.p.
1,2,3,4,5,6,7,8-Octa- hydrophenanthrene	Ni (Raney's) (6-37%?)		2-10	130
1,2,3,4,5,6,7,8-Octa- hydrophenanthrene	Copper chromite (6-44%?)			180-230(?)
1,2,3,4,5,6,7,8-Octa- hydrophenanthrene	AlCl ₃ (4.76%)		4	80
1,2,3,4,4a,9,10,10a-Octa- hydrophenanthrene	Copper chromite (6-44%?)			180-230(?)
1,2,3,4,4a,9,10,10a-Octa- hydrophenanthrene	Ni (Raney's) (6-37%?)		5	130 (?)
1,2,3,4,4a,9,10,10a-Octa- hydrophenanthrene	Ni (Raney's) (6-37%?)		19	130 (?)
9-Allylphenanthrene	Li (an excess) Ether (solvent) Alcohol (for demetalation)		30 for metala- tion	room
9-Allylphenanthrene	KOH (2.7%) C ₂ H ₅ OH (solvent) (81%)		4	b.p.
1-(3-Butenyl)-2-methyl-3,4- dihydrophenanthrene	30% Pd + 70% charcoal (6.75%)		2 at then 1 at	260-265 280-285

Fluorenes, Naphthalenes, Anthracenes, Phenanthrenes, Naphthacenes—*Continued*

Pressure (atms.)	Products		Refer- ences
	(Per cent by weight on original condensed aromatic) Isomers	Other Products	
	1,11b-Dihydro-7-benz[de]-anthrene		(225)
(CO ₂)	1,11b-Dihydro-7-benz[de]-anthrene (8%)	Naphthalene	(525)
1	2,2'-Dinaphthyl	1-Benzyl-naphthalene	(526)
1	9-Phenyl-9,14-dihydro-dibenz[ac]-anthracene		(57a)
100 (H ₂)	1,2,3,4,5,6,7,8-Octa-hydroanthracene	1,2,3,4,4a,9,9a,10-Octa-hydroanthracene	(450)
100 (H ₂)	1,2,3,4,4a,9,9a,10-Octa-hydroanthracene	1,2,3,4,5,6,7,8-Octa-hydroanthracene	(450)
100 (H ₂)	1,2,3,4,5,6,7,8-Octa-hydrophenanthrene (34.25%)	Fraction, b.p. 260–285° (5.5%)	(453)
		Fraction, b.p. 285–290° (13.5%)	
		Fraction, b.p. 295–305° (17.4%)	
1	1,2,3,4,5,6,7,8-Octa-hydrophenanthrene (40–44%)	1,2,3,4,5,6,7,8-Octa-hydroanthracene (44%)	(528)
		Dodecahydrotriphenylene (4.4–4.6%)	
		Yellow hydrocarbon, m.p. 320° (small %)	
		Fraction containing (?) 1,3-bis-(4-[9-octacenyl]butyl)benzene and (?) 6-(4-[9-octanthrenyl]butyl)-1,2,3,4-tetrahydronaphthalene (4.0% total)	
1	9-Benzohydryl-10-phenyl-anthracene		(44)
1	4,9,10-Triphenyl-1,9-(<i>o</i> -phenylene)-9,10-di-hydroanthracene		(640)
100–140 (N ₂)	1,2,3,4,4a,9,10,10a-Octa-hydrophenanthrene (3–4%)	1,2,3,4,5,6,7,8-Octa-hydrophenanthrene	(150)
100–140 (N ₂)	1,2,3,4,4a,9,10,10a-Octa-hydrophenanthrene	1,2,3,4,5,6,7,8-Octa-hydrophenanthrene	(150)
1	1,2,3,4,5,6,7,8-Octa-hydroanthracene (45%)	1,2,3,4,5,6,7,8-Octa-hydrophenanthrene (45%)	(528)
		Dodecahydrotriphenylene } (10%)	
		Other hydrocarbons }	
100–140 (N ₂)	1,2,3,4,5,6,7,8-Octa-hydrophenanthrene	1,2,3,4,4a,9,10,10a-Octa-hydrophenanthrene	(150)
100–140 (N ₂)	1,2,3,4,5,6,7,8-Octa-hydrophenanthrene (15%)	1,2,3,4,4a,9,10,10a-Octa-hydrophenanthrene	(150)
100–140 (N ₂)	1,2,3,4,5,6,7,8-Octa-hydrophenanthrene (28%)	1,2,3,4,4a,9,10,10a-Octa-hydrophenanthrene (66%)	(150)
		Other hydrophenanthrenes (traces)	
1	2,3-Dihydro-1-cyclopenta-[l]phenanthrene	9-Allylphenanthrene	(58)
1	9-Propenylphenanthrene (83.3%)		(47)
1	1-Butyl-2-methyl-phenanthrene		(95a)
1			

Table 40. Isomerization of Condensed Aromatics, Indanes, Indenes,

Condensed Aromatic	Reactants		Contact Time (hours)	Temp. (°C.)
	(Per cent by weight on aromatic + catalyst)	Catalyst		
1-(3-Butenyl)-2-methyl-3,4-dihydrophenanthrene	P ₂ O ₅	(50%)	6	140
1-(3-Butenyl)-2-methyl-3,4-dihydrophenanthrene	P ₂ O ₅			170
1-(3-Butenyl)-2-methyl-3,4-dihydrophenanthrene	H ₃ PO ₄ (prepared at 235° C.)	(15.9%)	48 at	100
	CH ₃ . CO ₂ H	(75.6%)	84 at	room
5,6,11,12-Tetraphenyl-naphthacene (Rubrene)	HI (gas)			
5,6,11,12-Tetraphenyl-naphthacene (Rubrene)	Solvents for rubrene			
5,6,11,12-Tetraphenyl-naphthacene (Rubrene)	HI (gas)			
5,6,11,12-Tetraphenyl-naphthacene (Rubrene)	Benzene (solvent)			
5,6,11,12-Tetraphenyl-naphthacene (Rubrene)	HI			
5,6,11,12-Tetraphenyl-naphthacene (Rubrene)	Solvents			
5,6,11,12-Tetraphenyl-naphthacene (Rubrene)	HI (gas)		0.5	room
5,6,11,12-Tetraphenyl-naphthacene (Rubrene)	Ether			
“Dihydorubrene, m.p. 249–250°”	Conc. solution sodium iso-		1	heated
Dimethylrubrene	amylate in isoamyl alcohol			
	Strong acid (H ₂ SO ₄)			
	Benzene (solvent)			

Table 41. Isomerization of

Reactants		Catalyst (Per cent by weight on aromatic + catalyst)	Contact Time (hours)	Temp. (°C.)
Aromatic-Cyclane				
1-Isopropyl-2-phenyl- cyclopropane “γ-Diphenyltruxane” (<i>cis</i> -form)		H ₂ SO ₄ , 90% H ₂ O, 10%	5	above 171
1,2,4-Triphenylcyclo- pentane			“aging for months”	room
1-Methyl-2,3,5-triphenylcyclo- pentane (liquid form)			“aging”	room
1,3-Dimethyl-2,4,5-triphenyl- cyclopentane (liquid form)			“aging”	room
1,2-Diphenyltetracyclo- hexylethane	Xylene (solvent)	(98%)	10 min.	100
1,2-Diphenyltetracyclo- hexylethane	40%-Sodium amalgam Ether (solvent) Later, CO ₂		6 (amalgam)	room

Fluorenes, Naphthalenes, Anthracenes, Phenanthrenes, Naphthacenes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original condensed aromatic)		Refer- ences
	Isomers	Other Products	
1	1-Butyl-2-methyl-phenanthrene (below 16%) 12a-Methyl-1,4,4a,11,12,12a-hexahydrochrysene (53%)	1-(3-Butenyl)-2-methyl-3,4-dihydrophenanthrene (below 16%)	(95a)
1	12a-Methyl-1,4,4a,11,12,12a-hexahydrochrysene		(95a)
1	12a-Methyl-1,4,4a,11,12,12a-hexahydrochrysene	1-(3-Butenyl)-2-methyl-3,4-dihydrophenanthrene	(95a)
1	12a-Methyl-1,4,4a,11,12,12a-hexahydrochrysene (crude, 3.5%)		
	Pseudo-rubrene		(34)
	Pseudo-rubrene (large %)	I ₂	(387)
	Pseudo-rubrene	I ₂	(388)
1	Pseudo-rubrene (6.25%)	I ₂ "Dihydorubrene, m.p. 230–231°" (14.4%) "Dihydorubrene, m.p. 249–250°" (35.0%)	(143)
1	"Dihydorubrene, m.p. 230–231°" (100%) Isomer (m.p. 271–272°) Isomer (m.p. 293–294°)		(143) (165)

Aromatic-Cyclane Hydrocarbons.

Pressure (atms.)	Products (Per cent by weight on original aromatic)		Refer- ences
	Isomers	Other Products	
1	1,1,2-Trimethylindane		(131a)
1	"α-Diphenyltruxane" (<i>trans</i> -form) (100%)		(568)
1	1,2,4-Triphenylcyclopentane (stable solid-form)		(403)
1	1-Methyl-2,3,5-triphenylcyclopentane (stable solid-form)		(1)
1	1,3-Dimethyl-2,4,5-triphenylcyclopentane (stable solid-form)		(1)
1	Isomer (m.p. 209°) (20%)		(474)
1	Isomer (m.p. 209°) (15%)	Phenyldicyclohexyl acetic acid (40%)	(474)

Table 42. Isomerization of

Reactants		Catalyst (Per cent by weight on aromatic + catalyst)	Contact Time (hours)	Temp. (°C.)
Aromatic-Cyclene				
1-(4-Phenylbutyl)cyclopentene-1	H ₂ SO ₄ , 90% H ₂ O, 10%		40-50 min.	9-10
1-(<i>o</i> -Biphenyl)yl)cyclopentene-1	AlCl ₃	(8%)	5	0
1-(β-1'-Naphthylethyl)cyclopentene-1	CS ₂	(86%)	24	0
	AlCl ₃	(8.1%)		
	CS ₂	(85.1%)		
1-Methyl-2-(β-1'-naphthylethyl)cyclopentene-1	AlCl ₃ CS ₂	(9.0%) (84.3%)	"overnight"	0
1-(β-9'-Phenanthrylethyl)-cyclopentene-1	AlCl ₃ CS ₂		12	room
1-(β-Phenethyl)cyclohexene-1	AlCl ₃ CS ₂		6	room
1-(β-Phenethyl)cyclohexene-1	AlCl ₃ CS ₂		18	room
1-(β-Phenethyl)cyclohexene-1	AlCl ₃ CS ₂	(9%) (85%)	24	room
1-(β-Phenethyl)cyclohexene-1	H ₂ SO ₄			room (?)
1-(β-Phenethyl)cyclohexene-1	H ₂ SO ₄ CH ₃ CO ₂ H	(14.9%) (77%)	1	b.p.
1-Methyl-2-benzylcyclohexene-1	AlCl ₃ CS ₂	(10.5%) (82.9%)	3 then "overnight"	at 0 room 0
1-Methyl-2-benzyl-4-isopropylcyclohexene-1	AlCl ₃		5	0
1-Methyl-2-(β-phenethyl)-cyclohexene-1	AlCl ₃ CS ₂			0
1-Isopropyl-2-(β-phenethyl)-4-methylcyclohexene-1	Conc. H ₂ SO ₄ (? Petroleum ether)			room (?)
1-(1'-Naphthyl)cyclohexene-1	AlCl ₃ CS ₂			0 (?)

AROMATIC-CYCLOPENTYLENE HYDROCARBONS

AROMATIC-CYCLOPENTYLENE HYDROCARBONS

Products	Products	Products	Products
by weight on original aromatic-Cyclopentylene Hydrocarbons	by weight on original aromatic-Cyclopentylene Hydrocarbons	by weight on original aromatic-Cyclopentylene Hydrocarbons	by weight on original aromatic-Cyclopentylene Hydrocarbons
1-Cyclopentyl-1,2,3,4-tetrahydronaphthalene (26)	1-Cyclopentyl-1,2,3,4-tetrahydronaphthalene (26)	1-Cyclopentyl-1,2,3,4-tetrahydronaphthalene (26)	1-Cyclopentyl-1,2,3,4-tetrahydronaphthalene (26)
9-Fluorylspirocyclopentane (52.5%)	9-Fluorylspirocyclopentane (52.5%)	9-Fluorylspirocyclopentane (52.5%)	9-Fluorylspirocyclopentane (52.5%)
<i>ci</i> - and <i>trans</i> -2,3,3a,10,11,11a-Hexahydro-1-cyclopenta[a]phenanthrene (83%)	<i>ci</i> - and <i>trans</i> -2,3,3a,10,11,11a-Hexahydro-1-cyclopenta[a]phenanthrene (83%)	<i>ci</i> - and <i>trans</i> -2,3,3a,10,11,11a-Hexahydro-1-cyclopenta[a]phenanthrene (83%)	<i>ci</i> - and <i>trans</i> -2,3,3a,10,11,11a-Hexahydro-1-cyclopenta[a]phenanthrene (83%)
May give instead (117)	May give instead (117)	May give instead (117)	May give instead (117)
2,3-Dihydro-spiro[benz[naphthene-1,1'-cyclopentane] (27.1%)	2,3-Dihydro-spiro[benz[naphthene-1,1'-cyclopentane] (27.1%)	2,3-Dihydro-spiro[benz[naphthene-1,1'-cyclopentane] (27.1%)	2,3-Dihydro-spiro[benz[naphthene-1,1'-cyclopentane] (27.1%)
2,3,3a,10,11,11a-Hexahydro-1-cyclopenta[a]phenanthrene (54.3%)	2,3,3a,10,11,11a-Hexahydro-1-cyclopenta[a]phenanthrene (54.3%)	2,3,3a,10,11,11a-Hexahydro-1-cyclopenta[a]phenanthrene (54.3%)	2,3,3a,10,11,11a-Hexahydro-1-cyclopenta[a]phenanthrene (54.3%)
Possibility of some:	Possibility of some:	Possibility of some:	Possibility of some:
1,2-Dihydro-spiro[3-benz[e]indene-3,1'-cyclopentane] (38.1%)	1,2-Dihydro-spiro[3-benz[e]indene-3,1'-cyclopentane] (38.1%)	1,2-Dihydro-spiro[3-benz[e]indene-3,1'-cyclopentane] (38.1%)	1,2-Dihydro-spiro[3-benz[e]indene-3,1'-cyclopentane] (38.1%)
3a-Methyl-2,3,3a,10,11,11a-Hexahydro-1-cyclopenta[a]phenanthrene (50%)	3a-Methyl-2,3,3a,10,11,11a-Hexahydro-1-cyclopenta[a]phenanthrene (50%)	3a-Methyl-2,3,3a,10,11,11a-Hexahydro-1-cyclopenta[a]phenanthrene (50%)	3a-Methyl-2,3,3a,10,11,11a-Hexahydro-1-cyclopenta[a]phenanthrene (50%)
Tetrahydrocyclopentophenylene (?) (49%)	Tetrahydrocyclopentophenylene (?) (49%)	Tetrahydrocyclopentophenylene (?) (49%)	Tetrahydrocyclopentophenylene (?) (49%)
1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (41%)	1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (41%)	1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (41%)	1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (41%)
<i>cis</i> -1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (large %)	<i>cis</i> -1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (large %)	<i>cis</i> -1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (large %)	<i>cis</i> -1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (large %)
<i>trans</i> -1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (small %)	<i>trans</i> -1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (small %)	<i>trans</i> -1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (small %)	<i>trans</i> -1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (small %)
Hydrindene-spirocyclopentane (smallest %)	Hydrindene-spirocyclopentane (smallest %)	Hydrindene-spirocyclopentane (smallest %)	Hydrindene-spirocyclopentane (smallest %)
1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (49%)	1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (49%)	1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (49%)	1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (49%)
1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (41%)	1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (41%)	1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (41%)	1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (41%)
1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (41%)	1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (41%)	1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (41%)	1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (41%)
9-Methyl-2,3-benz[e]cyclopentyl-nonene-2 (70%)	9-Methyl-2,3-benz[e]cyclopentyl-nonene-2 (70%)	9-Methyl-2,3-benz[e]cyclopentyl-nonene-2 (70%)	9-Methyl-2,3-benz[e]cyclopentyl-nonene-2 (70%)

Table 42. Isomerization of the

Aromatic-Cyclene	Reactants		Catalyst (Per cent by weight on aromatic + catalyst)	Contact Time (hours)	Temp. (°C.)
1-Methyl-2-(1'-naphthyl)- cyclohexene-1	AlCl ₃ CS ₂	(8.9%) (84.0%)	6.5	0	
1-Methyl-2-(2'-naphthyl- methyl)cyclohexene-1	AlCl ₃ CS ₂	(6.9%) (86.3%)	6	0	
1-(β-1'-Naphthylethyl)- cyclohexene-1	AlCl ₃ CS ₂	(8.1%) (85.1%)	7	0	
1-(β-1'-Naphthylethyl)- cyclohexene-1	AlCl ₃ CS ₂	(8.1%?) (85.1%?)		0	
1-Methyl-2-(β-1'-naphthyl- ethyl)cyclohexene-1	AlCl ₃ CS ₂	(8.7%) (84.0%)	7	0	
1-Methyl-2-(β-1'-naphthyl- <i>n</i> -propyl)cyclohexene-1	AlCl ₃ CS ₂	(7.6%) (85.6%)	21	0	
1-Methyl-2-(β-1'-naphthyl- ethyl)-4-isopropylcyclo- hexene-1	AlCl ₃ CS ₂	(12.3%) (77.4%)	24	0	
1-Methyl-2-(β-3'-ace- naphthylethyl)-cyclo- hexene-1	AlCl ₃ CS ₂	(7.0%) (85.7%)	21	0	
1-(β-9'-Phenanthrylethyl)- cyclohexene-1	AlCl ₃ CS ₂	(6.9%) (86.3%)	2-3	0	
1-Methyl-2-(β-9'-phen- anthrylethyl)cyclo- hexene-1	SnCl ₄ HCl	(3.9%)	48	room	
3-(β-Phenethyl)indene	C ₆ H ₆ AlCl ₃	(86.2%) (7.3%)	16	0	
3-(β-Phenethyl)indene	CS ₂ H ₂ SO ₄	(85.9%) (14.9%)	1	100	
2-Methyl-3-(β-phenethyl)- indene	CH ₃ · CO ₂ H AlCl ₃	(77%) (7.7%)	3	0	
2-Methyl-3-(β-1'-naphthyl- ethyl)indene	CS ₂ AlCl ₃	(85.7%) (8.3%)	3	0	
2-Methyl-3-(β-1'-naphthyl- isopropyl)indene (?)	CS ₂ (solvent) 1,4-Di-1-naphthyl-2,3- dimethylbutane (impurity)	(86.2%) (6.9%)	"overnight"	2-3	
2,5-Dimethyl-3-(β-1'- naphthylethyl)indene	AlCl ₃ CS ₂	(8.3%) (83.3%)	3	0	
2,6-Dimethyl-3-(β-1'- naphthylethyl)indene (88.9% pure ?)	AlCl ₃ CS ₂ (solvent) 1,4-Di-1-naphthyl- butane (impurity)	(8.3%) (83.3%) (0.93%)	3	0	
2,7-Dimethyl-3-(β-1'- naphthylethyl)indene	AlCl ₃ CS ₂	(8.3%) (83.3%)	3	0	
3-(β-1'-Naphthylethyl)-4- methyl-7-isopropylindene	AlCl ₃ CS ₂		4	0	

Aromatic-Cyclene Hydrocarbons—Continued

Pressure (atms)	Products (Per cent by weight on original aromatic)		Refer- ences
	Isomers	Other Products	
1	6b-Methyl-6b,7,8,9,10,- 10a-hexahydrofluor- anthrene (66%?)		(121)
1	7a,8,9,10,11,11a-Hexa- hydro-11a-methyl-3,4- benzofluorene (47%)		(113)
1	<i>cis</i> - and <i>trans</i> -1,2,3,4,4a,- 11,12,12a-Octahydro- chrysenes (14.2%)		(117)
1	7,8-Dihydrophenyl-7- spirocyclohexane (26.8%)		(117)
	<i>cis</i> -1,2,3,4,4a,11,12,12a- Octahydrochrysene (0.92%)		
	<i>trans</i> -1,2,3,4,4a,11,12,12a- Octahydrochrysene (0.16%)		
1	7,8-Dihydrophenyl-7-spiro- cyclohexane		(115)
	4a-Methyl-1,2,3,4,4a,11,- 12,12a-octahydro- chrysene (60%)		
1	4a,11-Dimethyl-1,2,3,4,4a,- 11,12,12a-octahydro- chrysene (72%)		(186)
1	2-Isopropyl-4a-methyl- 1,2,3,4,4a,11,12,12a-octa- hydrochrysene		(123)
1	8,9-Dihydro-2'-methyl- spiro[β -acenaphthin- dan-3,1'-cyclohexane]		(115)
1	Dihydrobenzanthrenespiro- cyclohexane (58%)		(250)
1	Dihydrobenzanthrenespiro- methylcyclohexane (?) (80%)		(45)
1	5,6,6a,11a-Tetrahydro- chrysofluorene (18%)	Resins	(117)
1	5,6,6a,11a-Tetrahydro- chrysofluorene (16%)	Resins	(117)
1	5,6,6a,11a-Tetrahydro- 11a-methylchryso- fluorene (82%)		(119)
1	11a-Methyl-5,6,6a,11a- tetrahydro-11-naphtho- [2,1-a]fluorene (27.2%)		(25)
1	6,11a-Dimethyl-5,6,6a,- 11a-tetrahydro-11- naphtho[2,1-a]fluorene (?)		(25)
1	8,11a-Dimethyl-5,6,6a,- 11a-tetrahydro-11- naphtho[2,1-a]fluorene (18.9%)		(25)
1	9,11a-Dimethyl-5,6,6a,- 11a-tetrahydro-11- naphtho[2,1-a]fluorene (5.0%)		(25)
1	10,11a-Dimethyl-5,6,6a,- 11a-tetrahydro-11- naphtho[2,1-a]fluorene (19.1%)		(25)
1	2,3-Dihydro-4'-isopropyl- 7'-methyl-spiro[benzo- naphthene-1,1'-indan]		(119)

Table 42. Isomerization of the

Reactants		Catalyst (Per cent by weight on aromatic + catalyst)	Contact Time (hours)	Temp. (°C.)
Aromatic-Cyclene				
2-Methyl-3-(β -[5,6,7,8-tetrahydro-1-naphthyl]ethyl)-indene	AlCl ₃ CS ₂	(8.3%) (83.3%)	3	0
2-Methyl-3-(β -[5,6,7,8-tetrahydro-1-naphthyl]ethyl)-indene	H ₂ SO ₄ CH ₃ . CO ₂ H			100
2,4-Dimethyl-3-(β -[5,6,7,8-tetrahydro-1-naphthyl]ethyl)-7-isopropylindene			3	0
2,4-Dimethyl-3-(β -[5,6,7,8-tetrahydro-1-naphthyl]ethyl)-7-isopropylindene	H ₂ SO ₄ CH ₃ . CO ₂ H			100
1-(β -Phenethyl)-3,4-dihydronaphthalene	AlCl ₃ CS ₂	(8.4%) (84.9%)	6	0
2-(β -Phenethyl)- Δ^2 -octalin	AlCl ₃ CS ₂	(8.5%) (84.8%)	4 at then	0
2-(β -Phenethyl)- <i>cis</i> - Δ^2 -octalin	AlCl ₃ CS ₂	(8.5%) (84.5%)	"overnight" at 3 at then	room 0
2-(β - <i>o</i> -Tolylethyl)- Δ^2 -octalin	AlCl ₃ CS ₂	(9.5%) (83.8%)	several at "mixed" at then	room 0
1-(β -Phenethyl)-2-methyl-3- α -naphthindene	AlCl ₃ CS ₂	(6.9%) (86.3%)	"overnight" at 4	room 0
1,2-Dihydro-4-(β -phenethyl)-phenanthrene	AlCl ₃ CS ₂	(12.8%) (80.8%)	12	0
1-(β -Phenethyl)-3,4-dihydrophenanthrene	AlCl ₃ CS ₂	(6.9%) (86.3%)	0.5 at then "overnight" at	0 5
1-(β - <i>o</i> -tolylethyl)-3,4-dihydrophenanthrene	AlCl ₃ CS ₂			0 (?)
1-(β - <i>p</i> -tolylethyl)-3,4-dihydrophenanthrene	AlCl ₃ CS ₂			0 (?)

MR ONT DRUGS MR ONT DRUGS MR ONT DRUGS MR ONT DRUGS MR ONT DRUGS MR ONT DRUGS MR ONT DRUGS MR ONT DRUGS MR ONT DRUGS MR ONT DRUGS

Propylbenzene Cyclohexene Hydrocarbons Propylbenzene Cyclohexene Hydrocarbons Propylbenzene Cyclohexene Hydrocarbons Propylbenzene Cyclohexene Hydrocarbons

Products		Products		Products		Products	
by weight on original		by weight on original		by weight on original		by weight on original	
Other Products		Other Products		Other Products		Other Products	
ethyl-3,4,5,10,-	(82.5%)	1,2-Dimethyl-3,4,5,10,-	(82.5%)	1,2-Dimethyl-3,4,5,10,-	(82.5%)	1,2-Dimethyl-3,4,5,10,-	(82.5%)
hexahydrophen-		10a-hexahydrophen-		10a-hexahydrophen-		10a-hexahydrophen-	
ene		threne		threne		threne	
yl-2-phenyl-	(82.5%)	1-Methyl-2-phenyl-	(82.5%)	1-Methyl-2-phenyl-	(82.5%)	1-Methyl-2-phenyl-	(82.5%)
lbenzene		propylbenzene		propylbenzene		propylbenzene	
yl-2-phenyl-	(82.5%)	1-Methyl-3-phenyl-	(82.5%)	1-Methyl-2-phenyl-	(82.5%)	1-Methyl-2-phenyl-	(82.5%)
lbenzene		propylbenzene		propylbenzene		propylbenzene	
yl-2-benzyl-	(82.5%)	1-Methyl-2-benzyl-	(82.5%)	1-Methyl-2-benzyl-	(82.5%)	1-Methyl-2-benzyl-	(82.5%)
lbenzene		propylbenzene		propylbenzene		propylbenzene	
yl-2-benzyl-	(82.5%)	1-Methyl-2-benzyl-	(82.5%)	1-Methyl-2-benzyl-	(82.5%)	1-Methyl-2-benzyl-	(82.5%)
lbenzene		propylbenzene		propylbenzene		propylbenzene	

Table 44. Possibilities of Hydrocarbon Isomerization as Illustrated by the Known Examples to Date.

("Iso" denotes a branched structure)

1. *n*-Alkane → *Iso*-alkane with shorter chain
2. *n*-Alkane → 2-Methylalkane with shorter chain
3. *n*-Alkane → 3-Methylalkane with shorter chain
4. *n*-Alkane → 2,4-Dimethylalkane with shorter chain
5. *n*-Alkane → 3,3-Dimethylalkane with shorter chain
6. *n*-Alkane → 2,2,3-Trimethylalkane with shorter chain
7. *Iso*-alkane → *n*-Alkane with longer chain
8. 2-Methylalkane → *n*-Alkane with longer chain
9. 2-Methylalkane → 3-Methylalkane
10. 2-Methylalkane → 2,3-Dimethylalkane with shorter chain
11. 3-Methylalkane → 2-Methylalkane
12. 2,2-Dimethylalkane → 2-Methylalkane with longer chain
13. 2,2-Dimethylalkane → 2,3-Dimethylalkane
14. 2,3-Dimethylalkane → 2-Methylalkane with longer chain
15. 2,3-Dimethylalkane → 2,2-Dimethylalkane
16. 2,4-Dimethylalkane → 2,3-Dimethylalkane
17. *n*-Alkene → Geometrical isomer (*cis* or *trans*)
18. *n*-Alkene → *n*-Alkene with shifted double-bond
19. *n*-Alkene → *Iso*-alkene
20. *n*-Alkene → Cyclane
21. *Iso*-alkene → *Iso*-alkene with shifted double-bond
22. 2-Methylalkene-1 → 3-Methylalkene-1
23. 2-Methylalkene-1 → 2-Methylalkene-2
24. 3-Methylalkene-1 → 2-Methylalkene-1
25. 3-Methylalkene-1 → 2-Methylalkene-2
26. 2-Methylalkene-2 → 2-Methylalkene-1
27. 2-Methylalkene-2 → 3-Methylalkene-1
28. 3-Methylalkene-2 → 2-Ethylalkene-1 by shift of double-bond only
29. 2-Ethylalkene-1 → 3-Methylalkene-2 by shift of double-bond only
30. 2,3-Dimethylalkene-1 → 2,3-Dimethylalkene-2
31. 2,3-Dimethylalkene-2 → 2,3-Dimethylalkene-1
32. *Iso*-alkene → *Iso*-alkene with shifted methyl-group
33. 2,3-Dimethylalkene-1 → 3,3-Dimethylalkene-1
34. *Iso*-alkene → *Iso*-alkene with shifted double-bond and shifted methyl-group
35. 3-Methylalkene-2 → 2-Methylalkene-1
36. 2,3-Dimethylalkene-2 → 3,3-Dimethylalkene-1
37. *Iso*-alkene → Alkyl cyclane
38. Non-allenic, unconjugated *n*-alkadiene → Conjugated *n*-alkadiene by shift of one double-bond only
39. Non-allenic, unconjugated *n*-alkadiene → Conjugated *n*-alkadiene by shift of both double-bonds
40. Non-allenic, unconjugated *n*-alkadiene → Non-allenic, unconjugated *iso*-alkadiene with shorter chain
41. Non-allenic, unconjugated *n*-alkadiene → *n*-Alkyne
42. Non-allenic, conjugated *n*-alkadiene → Non-allenic, unconjugated *n*-alkadiene
43. Non-allenic, conjugated *n*-alkadiene → Conjugated *n*-alkadiene
44. Non-allenic, unconjugated *iso*-alkadiene → Non-allenic, unconjugated *iso*-alkadiene by shift of one double-bond only
45. Non-allenic, unconjugated *iso*-alkadiene → Conjugated *iso*-alkadiene by shift of one double-bond only
46. Non-allenic, unconjugated *iso*-alkadiene → Conjugated *iso*-alkadiene by shift of both double-bonds
47. Non-allenic, unconjugated *iso*-alkadiene → Polyalkyl cyclene
48. Non-allenic, conjugated *iso*-alkadiene → *Iso*-allenic
49. *n*-Allenic → Conjugated *n*-alkadiene

Table 44—Continued

50. *n*-Allenic → *n*-Alkyne
51. *Iso*-allenic → Conjugated *iso*-alkadiene
52. *Iso*-allenic → Conjugated *iso*-alkadiene with shifted methyl-group
53. *Iso*-allenic → *Iso*-alkyne
54. *Iso*-alkatriene-1,2,3 → *Iso*-alken-3-yne-1
55. *Iso*-alkapolyene → Less-conjugated *iso*-alkapolyene
56. *Iso*-alkapolyene → More-conjugated *iso*-alkapolyene
57. Partly - conjugated *iso*-alkapolyene → Conjugated polyalkyl - monoalkylidene cyclene
58. Partly-conjugated *iso*-alkapolyene → Polyalkyl hexahydronaphthalene
59. Partly - conjugated *iso* - alkapolyene → Unconjugated polyalkyl - monoalkenyl cyclene
60. Partly - conjugated *iso*-alkapolyene → "Unconjugated" alkyl-*iso*alkadienyl cyclene
61. Unconjugated *iso*-alkapolyene → "Unconjugated" polyalkyl-monoalkenyl cyclene
62. *n*-Alkyne → *n*-Alkyne with shifted triple-bond
63. *n*-Alkyne → *n*-Allenic
64. *n*-Alkyne → Non-allenic, conjugated *n*-alkadiene
65. *Iso*-alkyne → Conjugated *iso*-alkadiene
66. *Iso*-alkyne → *Iso*-allenic
67. Unconjugated *n*-alkadiyne → Conjugated *n*-alkadiyne
68. Unconjugated *iso*-alkapolyne → Conjugated *iso*-alkapolyenepolyne
69. *n*-Cyclane → *n*-Alkene
70. *n*-Cyclane → Alkyl cyclane of smaller ring-size
71. Alkyl cyclane → *n*-Alkene
72. Alkyl cyclane → *Iso*-alkene
73. Alkyl cyclane → Polyalkyl cyclane of smaller ring-size
74. Alkyl cyclane → Stable multiplanar-form with "same" ring-size
75. Alkyl cyclane → Polyalkyl cyclane with same ring-size
76. *Iso*alkyl cyclane → Polyalkyl cyclane with same ring-size
77. Alkylcyclane → Alkyl cyclane of larger ring-size but with smaller alkyl
78. Alkyl cyclane → Polyalkyl cyclane of larger ring-size but with smaller alkyls
79. Alkyl cyclane → *n*-Cyclane of larger ring-size
80. Dialkyl cyclane → Polyalkyl cyclane with smaller alkyls
81. Dialkyl cyclane → Alkyl cyclane of larger ring-size
82. Polyalkyl cyclane → Stable geometrical-form with same ring-size
83. Polyalkyl cyclane → Polyalkyl cyclane of same ring-size but *ortho*-resubstituted
84. Polyalkyl cyclane → Polyalkyl cyclane of same ring-size but *meta*-resubstituted
85. Polyalkyl cyclane → Polyalkyl cyclane of same ring-size but *para*-resubstituted
86. Alkenyl cyclane → Alkenyl cyclane with shifted double-bond
87. Alkenyl cyclane → Conjugated *n*-alkadiene
88. Alkenyl cyclane → Conjugated *iso*-alkadiene
89. Alkenyl cyclane → Alkyl cyclene
90. *Iso*alkenyl cyclane → *Iso*alkyl cyclene
91. Alkyl-*iso*alkenyl cyclane → Alkyl-*iso*alkyl cyclene
92. Alkadienyl cyclane → Alkynyl cyclane
93. Alkadienyl cyclane → Alkenyl cyclene
94. Alkynyl cyclane → Alkynyl cyclane with shifted triple-bond
95. Alkynyl cyclane → Alkadienyl cyclane
96. Dicyclanyl → Form with "same" ring-sizes but different stability
97. Spirane → Bicyclane
98. *n*-Bicyclane → Stable (*trans*) form with same ring-sizes
99. *n*-Bicyclane → Polyalkyl bicyclane with both rings smaller
100. *n*-Bicyclane → *n*-Bicyclane with one ring larger
101. Alkyl bicyclane → Stable (*trans*) form with same ring-sizes
102. Alkyl bicyclane → Polyalkyl bicyclane with one ring smaller
103. Alkyl-alkenyl bicyclane → Polyalkyl-monoalkenyl cyclene
104. Alkyl-alkenyl bicyclane → Polyalkyl cyclodiene
105. Polyalkyl-monoalkenyl bicyclane → *Iso*-alkatriene
106. Polyalkyl-monoalkenyl bicyclane → Alkyl-*iso*alkenylcyclene with new alkyl
107. Polyalkyl-monoalkenyl bicyclane → Polyalkyl cyclodiene with new alkyls

Table 44—Continued

108. Polyalkyl-monoalkenyl bicyclane → Polyalkyl-monoalkenyl bicyclane *via* Wagner rearrangement
109. Polyalkyl-monoalkenyl bicyclane → Polyalkyl bicyclene with one more alkyl
110. Polyalkyl-monoalkenyl bicyclane → Polyalkyl bicyclene with one more alkyl, *via* Wagner rearrangement
111. Polyalkyl-monoalkenyl bicyclane → Polyalkyl bicyclene with different ring-sizes and one more alkyl
112. Tricyclane → Stable (*trans*) form with same ring-sizes and same ring-attachment
113. Tricyclane → Labile (*cis*) form with same ring-sizes and same ring-attachment
114. Tricyclane → Tricyclane with same ring-sizes and different ring-attachment
115. Polyalkyl tricyclane → Polyalkyl-monoalkenyl bicyclane with loss of one alkyl
116. Polyalkyl tricyclane → Polyalkyl bicyclene
117. Polyalkyl tricyclane → Polyalkyl bicyclene with a shifted alkyl-group
118. Alkyl cyclene → Conjugated *n*-alkadiene
119. Alkyl cyclene → Alkylidene cyclane
120. Polyalkyl cyclene → Polyalkyl cyclene with shifted double-bond
121. Partly-conjugated alkyl-isoalkapolyenyl cyclene → "Unconjugated" polyalkyl-isoalkyl bicyclodiene
122. Unconjugated alkenyl cyclene → Conjugated alkenyl cyclene
123. Alkenyl cyclene → *n*-Bicyclene with removal of side-chain double-bond
124. Alkenyl cyclene → *n*-Bicyclene with removal of ring double-bond
125. Alkyl-alkenyl cyclene → Alkyl bicyclene with removal of ring double-bond and shift of the other double bond
126. *d*-Rotatory alkyl-isoalkenyl cyclene → *Racemic* alkyl-isoalkenyl cyclene
127. Alkyl-isoalkenyl cyclene → Alkyl-isoalkenyl cyclene with shifted double-bond in side-chain
128. Alkyl-isoalkenyl cyclene → Alkyl-isoalkenyl cyclene with shifted double-bond in ring
129. Alkyl-isoalkenyl cyclene → Alkyl-isoalkyl cyclodiene
130. Isoalkenyl-isoalkapolyenyl cyclene → Polyalkyl-isoalkenyl bicyclene
131. Polyalkyl-isoalkapolyenyl cyclene → More-conjugated polyalkyl-isoalkapolyenyl cyclene
132. Polyalkyl-isoalkapolyenyl cyclene → Less-conjugated polyalkyl-isoalkapolyenyl cyclene
133. Alkynyl cyclene → Alkyl benzene
134. Polyalkyl cyclodiene → Polyalkyl cyclodiene with one shifted double-bond in ring
135. Polyalkyl-monoalkenyl cyclodiene → Polyalkyl benzene
136. *n*-Bicyclene → *n*-Bicyclene with shifted double-bond
137. Polyalkyl bicyclene → Conjugated *iso*-alkapolyene
138. Polyalkyl bicyclene → Alkyl-isoalkenyl cyclene
139. Polyalkyl bicyclene → Conjugated polyalkyl cyclodiene
140. Polyalkyl bicyclene → Polyalkyl-monoalkenyl bicyclane *via* double Wagner-rearrangement
141. *n*-Tricyclene → *n*-Tricyclene with shifted double-bond
142. Polyalkyl tricyclene → Polyalkyl bicyclodiene
143. Polyalkyl tricyclene → Bicyclic isomer
144. Polyalkyl tricyclene → Tricyclic isomer
145. Polyalkyl-(*iso*?)alkenyl tricyclene → Polyalkyl tetracyclene
146. Polyalkyl tetracyclodiene → Polyalkyl tetracyclodiene with shifted double-bonds
147. Polyalkyl pentacyclene → Polyalkyl pentacyclene with shifted double-bond
148. Aliphatic sesquiterpene → Monocyclic sesquiterpene
149. Aliphatic sesquiterpene → Bicyclic sesquiterpene
150. Monocyclic sesquiterpene → Bicyclic sesquiterpene
151. Bicyclic sesquiterpene → Monocyclic sesquiterpene
152. Bicyclic sesquiterpene → Isomeric bicyclic sesquiterpene
153. Bicyclic sesquiterpene → Tricyclic sesquiterpene
154. Tricyclic sesquiterpene → Bicyclic sesquiterpene
155. Monocyclic diterpene → Bicyclic diterpene
156. Bicyclic diterpene → Tricyclic diterpene
157. Tricyclic diterpene → Tetracyclic diterpene
158. Tetracyclic diterpene → Isomeric tetracyclic diterpene
159. Alkyl benzene → Alkenyl cyclodiene

Table 44—Continued

160. Alkyl benzene → Polyalkyl benzene
161. Polyalkyl benzene → Polyalkyl benzene with *ortho* resubstitution
162. Polyalkyl benzene → Polyalkyl benzene with *meta* resubstitution
163. Polyalkyl benzene → Polyalkyl benzene with *meta* resubstitution and formation of "secondaried" alkyl
164. Polyalkyl benzene → Polyalkyl benzene with *meta* resubstitution and formation of "tertiaried" alkyl
165. Polyalkyl benzene → Polyalkyl benzene with *para* resubstitution
166. Hexaphenylethane → *p*-Benzohydryltetraphenylmethane
167. *Racemic*-1,2-dialkyl-1,2-diaryl ethane → *Meso*-1,2-dialkyl-1,2-diaryl ethane
168. *Meso*-1,2-dialkyl-1,2-diaryl ethane → *Racemic*-1,2-dialkyl-1,2-diaryl ethane
169. Alkenyl benzene → Alkenyl benzene with shifted double-bond
170. Alkenyl benzene → Alkyl tetralin
171. *Iso*alkenyl benzene → Polyalkyl indane
172. Alkyl-alkenyl benzene → Alkyl-alkenyl benzene with shifted double-bond
173. Dialkenyl benzene → Dialkenyl benzene with one shifted double-bond
174. Dialkenyl benzene → Dialkenyl benzene with two shifted double-bonds
175. Diphenylethylene → Geometrical isomer (*cis* or *trans*)
176. Phenyl-(*o*-biphenyl)-ethylene → Phenyldihydrophenanthrene
177. Polyaryl propene → Polyaryl propene with shifted double-bond
178. Polyaryl propene → Polyaryl indane
179. Polyaryl propene → Polyaryl indane with shifted phenyl-group
180. Polyaryl butene → Stable form
181. Polyaryl butene → Polyaryl butene with shifted double-bond
182. Polyaryl butene → Polyaryl butene with shifted double-bond and two shifted phenyl-groups
183. Polyaryl butene → Polyaryl cyclobutane
184. Polyaryl butene → Alkyl-polyaryl indane
185. Polyaryl butene → Aralkyl-polyaryl indane
186. Alkyl-diaryl pentene → Polyalkyl-monoaryl indane
187. Alkadienyl benzene → Stable form
188. Alkadienyl benzene → Alkynyl benzene
189. Diaryl butadiene → Stable form
190. Polyaryl butadiene → Arylmethylene-polyaryl indane
191. Polyaryl butadiene → 1-Arylmethyl-polyaryl indene
192. Polyaryl butadiene → 1-Methyl-polyaryl indene
193. Diaryl-biphenylene butadiene → Methyl-aryl-biphenylene indene
194. *d*-Rotatory polyaryl allene → *Racemic* polyaryl allene
195. Polyaryl allene → Polyaryl indene
196. Polyaryl allene → Polyaryl 3- α -naphthindene
197. Polyalkyl-polyaryl diallenic → Polyalkyl-polyaryl biindene
198. Polyaryl alkapolyene → Stable form
199. *ar*-Conjugated polyaryl trivinylmethane → *ac*-Conjugated isomer
200. Alkynyl benzene → Alkadienyl benzene
201. Alkynyl benzene → Alkynyl benzene with shifted triple-bond
202. Polyaryl alkyne-2 → Polyaryl alkadiene-1,3
203. Polyaryl unconjugated-alkadiyne → Stable isomer
204. Polyaryl unconjugated-*polyiso*-alkadiyne → Stable isomer
205. Polyaryl unconjugated-*polyiso*-alkadiyne → Polyaryl conjugated-*polyiso*-alkapolyene
206. 1-*Iso*alkenylidene indene → Polyalkyl dihydrofluorene
207. 1-Aryl indene → 3-Aryl indene
208. 3-Aryl indene → 2-Aryl indene
209. 1-Aryl-3-*iso*alkyl indene → 1-*Iso*alkyl-3-aryl indene
210. 1,2-Diaryl indene → 3,2-Diaryl indene
211. 1-(A-Arylmethylene)-3-(B-arylmethyl)indene → 1-(B-Arylmethylene)-3-(A-arylmethyl) indene
212. 1,1,3-Triaryl indene → 1,2,3-Triaryl indene
213. 1,2,3-Triaryl indene → 3,2,1-Triaryl indene
214. 1-Diphenylmethylene-indene → 3-Benzhydrylindene
215. 1,3-Dibenzylidene-indane → 1-Benzylidene-3-benzylindene

Table 44—Continued

216. 1,4-Dihydronaphthalene → 1,2-Dihydronaphthalene
217. 1-Alkyl naphthalene → 2-Alkyl naphthalene
218. 1-Alkylidene-2-alkyl-1,4-dihydronaphthalene → 1,2-Dialkyl naphthalene
219. 1,6-Dialkyl naphthalene → 2,6-Dialkyl naphthalene
220. 1-Alkenyl naphthalene → 1-Alkenyl naphthalene with shifted double-bond in side-chain
221. 1-Isoalkenyl-1,2,3,4-tetrahydronaphthalene → 1-Isoalkylidene-1,2,3,4-tetrahydronaphthalene
222. 1-Aryl naphthalene → 2-Aryl naphthalene
223. 1-Benzyl naphthalene → Dihydrobenzanthrene
224. 1,2,3-Triaryl naphthalene → 9-Aryl-9,14-dihydro-dibenz[ac]anthracene
225. *unsym.*-Octahydroanthracene → *sym.*-Octahydroanthracene
226. *sym.*-Octahydroanthracene → *unsym.*-Octahydroanthracene
227. *sym.*-Octahydroanthracene → *sym.*-Octahydrophenanthrene
228. Polyaryl anthracene → Polyaryl 1,9-(*o*-phenylene)-9,10-dihydroanthracene with "loss" of one aryl-group
229. Aryl-9-diphenylmethylene 9,10-dihydroanthracene → Aryl-9-diphenylmethyl anthracene with "gain" of one aryl-ring
230. *unsym.*-Octahydrophenanthrene → *sym.*-Octahydrophenanthrene
231. *sym.*-Octahydrophenanthrene → *sym.*-Octahydroanthracene
232. *sym.*-Octahydrophenanthrene → *unsym.*-Octahydrophenanthrene
233. 9-Alkenyl phenanthrene → 9-Alkenyl phenanthrene with shifted double-bond in side-chain
234. 9-(Alk-2-enyl)phenanthrene → 2,3-Dihydro-1-cyclopenta[l]phenanthrene
235. Alkyl-alkenyl dihydrophenanthrene → Dialkyl phenanthrene
236. Alkyl-1-(alk-3-enyl) dihydrophenanthrene → Alkyl hexahydrochrysene
237. Polyaryl naphthacene → Phenylene isomers with less arylation
238. Poly-cyclohexyl-and-polyaryl ethane → Stable isomer with rearrangement of structure
239. Isoalkyl-aryl cyclane → Polyalkyl indane
240. Polyaryl cyclane → Stable form
241. Alkyl-polyaryl cyclane → Stable form
242. Polyalkyl-polyaryl cyclane → Stable form
243. Polyalkyl-polyaryl cyclane of condensed (dehydrogenated) type → Stable form
244. (4-Phenylbutyl)cyclopentene → 1-Cyclopentyl-1,2,3,4-tetrahydronaphthalene
245. *o*-Biphenyl cyclopentene → Tetracyclic spirane
246. β -1'-Naphthylethyl cyclopentene → Hexahydro-1-cyclopenta[a]phenanthrene
247. Alkyl- β -1'-naphthylethyl cyclopentene → Alkyl hexahydro-1-cyclopenta[a]phenanthrene
248. β -9'-Phenanthrylethyl cyclopentene → Tetrahydrocyclopentenotriphenylene
249. Alkyl-benzyl cyclohexene → Alkyl 2,3-benzbicyclo[3.3.1]nonene-2
250. Polyalkyl-benzyl cyclohexene → Polyalkyl 2,3-benzbicyclo[3.3.1]nonene-2
251. β -Phenethyl cyclohexene → *unsym.*-Octahydrophenanthrenes
252. β -Phenethyl cyclohexene → Hydrindene-spirocyclohexane
253. Alkyl- β -phenethyl cyclohexene → Alkyl *unsym.*-octahydrophenanthrene
254. Polyalkyl- β -phenethyl cyclohexene → Polyalkyl *unsym.*-octahydrophenanthrene
255. Alkyl-1'-naphthyl cyclohexene → Alkyl hexahydrofluoranthene
256. Alkyl-2'-naphthylmethyl cyclohexene → Alkyl hexahydro-3,4-benzofluorene
257. β -1'-Naphthylethyl cyclohexene → Octahydrochrysene
258. β -1'-Naphthylethyl cyclohexene → Dihydro-spiro[benzonaphthene-1,1'-cyclohexane]
259. Alkyl- β -1'-naphthylethyl cyclohexene → Alkyl octahydrochrysene
260. Polyalkyl- β -1'-naphthylethyl cyclohexene → Polyalkyl octahydrochrysene
261. Alkyl- β -1'-naphthylpropyl cyclohexene → Polyalkyl octahydrochrysene
262. Alkyl- β -3'-acenaphthylethyl cyclohexene → Alkyl pentacyclic spirane
263. β -9'-Phenanthrylethyl cyclohexene → Pentacyclic spirane
264. Alkyl- β -9'-phenanthrylethyl cyclohexene → Alkyl pentacyclic spirane
265. β -Phenethyl indene → Tetrahydrochrysofluorene
266. Alkyl- β -phenethyl indene → Alkyl tetrahydrochrysofluorene
267. Alkyl- β -1'-naphthylethyl indene → Alkyl tetrahydronaphtho[2,1-a]fluorene
268. Polyalkyl- β -1'-naphthylethyl indene → Polyalkyl pentacyclic spirane

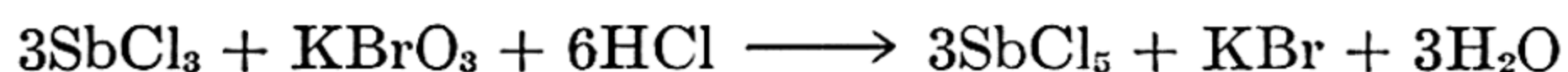
[illegible]

Appendix I

The following extended translation of Moldavsky and Livschitz's fundamental work on iso-alkane determination [*J. Gen. Chem. (U. S. S. R.)*, 5, 422-431 (1935)] is submitted by the present authors for the perusal of readers interested in the quantitative estimation of alkane isomers by means of antimony pentachloride. The basis of their method consists of an x -fold chlorination of alkane molecules.



The extent of substitution ($x=1$ to 6) depends both upon the degree of chain branching in the alkane and upon the total time of reaction. The amount of antimony trichloride formed, which is a measure of the chlorination, is determined by titration against a standard solution of potassium bromate,



Isomerization of Hydrocarbons. *I. The Chlorination of Hexane and Octane Isomers by Means of Antimony Pentachloride as a Quantitative Method of their Determination.* B. L. Moldavsky and S. E. Livschitz, State Institute of High Pressure.

In studies of n -hexane and n -octane isomerization, we found it necessary to develop an analytical method for small quantities of these hydrocarbons and their isomers. The present methods for iso-alkane determination are based on the large difference in reactivities of hydrogen attached to a tertiary carbon atom and hydrogen attached to primary or secondary carbon atoms. The nitration procedure of M. Konovalov should be noticed first among these methods.

This method has been used by other investigators to study the structure of petroleum hydrocarbons. Markovnikov and his pupils have conducted particularly large investigations in a study of Caucasian oils. S. Nametkin and S. Nefontova^{31c,a} have recently applied Konovalov's method in a study of the structure of alkanes from Grozny and American sources. In spite of the big role of nitration observed by Konovalov in oil-structure studies, his method cannot be used quantitatively. It is an objectionably incomplete nitration that always leaves a large amount of unreacted hydrocarbons.

Among the different attempts to determine iso-structure hydrocarbons, most attention probably should be given to Schaarschmidt's method^{500, 500a, 574d} of chlorination by SbCl_5 . The ability of antimony pentachloride to chlorinate organic compounds has been known a long time, and it is used for such purposes in many cases.^{257b}

V. Meyer and F. Müller^{375a} studied chlorination by SbCl_5 in the aliphatic series. By using equimolecular quantities of polyhalogen derivatives of the methane series hydrocarbons (C_2H_6 , C_3H_8 , C_4H_{10}) and SbCl_5 , they found that the second halogen is always placed in proximity to the first. Schaarschmidt studied the action of SbCl_5 on alkanes and "naphthenes." His experiments have demonstrated that the *n*-alkanes, the "naphthenes" without side-chains, and iso-compounds with quaternary carbon atoms are chlorinated very slowly at room temperature and rapidly only at temperatures above 60° . But the iso-alkanes and the "naphthenes" with side-chains, i.e., the compounds containing hydrogen at a tertiary carbon atom, are rapidly chlorinated by SbCl_5 at room temperature and even at 0° . According to this author, it is possible to recognize 0.1 per cent of iso-compounds in *n*-alkanes by means of SbCl_5 . Obviously, the material to be investigated must not contain any alkenes or aromatic hydrocarbons, which are easily chlorinated by SbCl_5 . The action of SbCl_5 on iso-compounds gives colorless or slightly yellow crystalline precipitates, which contain two molecules of SbCl_5 for one of the iso-compound. His experiments on the chlorination of iso- and *n*-alkanes have shown that an induced chlorination of the latter occurs and seriously interferes with the quantitative analysis.

Deciding to use Schaarschmidt's method for the analysis of mixtures of isomeric hexanes and octanes, we started a study of the chlorination effected by SbCl_5 . The serious difficulties of Schaarschmidt's method are, first, induced chlorination of *n*-alkanes and, secondly, the absence of a quantitative check on the course of the chlorination. Therefore, it was decided to conduct this reaction in the presence of solvents and to control the amount of SbCl_5 used in the chlorination. Since SbCl_3 is formed during chlorination of the hydrocarbons, a determination of either the SbCl_5 used or SbCl_3 formed gives the extent of iso-compound chlorination. We used the iodometric method of Szebellédy^{575b} in order to determine the SbCl_5 , and that of Györy^{590a} for SbCl_3 . The methods of determination of SbCl_5 and SbCl_3 gave satisfactory results when conducted in water, chloroform, or carbon tetrachloride solution.

Materials Used and Method of Operation

The following hydrocarbons were synthesized: 2-methylbutane, *n*-hexane, 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane, *n*-octane, 4-methylheptane, and 2,5-dimethylhexane. With the exception of 2,5-dimethylhexane, all iso-compounds were prepared by reduction of our synthesized, corresponding tertiary alcohols with hydrogen under pressure and MoS_2 as catalyst.^{380a} The *n*-hexane, *n*-octane, and 2,5-dimethylhexane were prepared by the Würtz reaction. The resulting *n*-alkanes contained a small amount of isomers due probably to the presence of these isomers in the original *n*-propyl and butyl alcohols. In order to remove such isomers, the *n*-alkanes were treated with 10 weight-per cent of SbCl_5 for 2-3 hours at room temperature, washed with alkali and water, dried, and distilled over metallic sodium. Iso-compounds obtained by the reduction of tertiary alcohols were treated several times with sulfuric acid (sp. gr. 1.84), washed with alkali and water, and also distilled over sodium. The synthesized hydrocarbons had the following boiling points: 2-methylbutane $29-31.5^\circ$, 2-methylpentane $60-61^\circ$, 3-

methylpentane 62-63°, 2,3-dimethylbutane 57-58.5°, *n*-hexane 68-69°, 4-methylheptane 117-118.5°, 2,5-dimethylhexane 108-109°, and *n*-octane 125-127°.

The following methods were used in the experiments. Carefully cleaned test tubes were placed in a large vessel containing snow or ice. One ml. of SbCl_5 solution in CCl_4 or CHCl_3 and of various concentrations was placed in the carefully cleaned and dried test tubes by means of a pipette. The concentration of SbCl_5 was determined by titration according to Szebellédy's method. The test tubes were closed by rubber stoppers supplied with capillary tubing. After standing in snow for 5 minutes, 0.1-0.2 ml. of 0.5-2.0*N* solution of iso-compound in chloroform or carbon tetrachloride was added to the test tubes by means of a micro-pipette. After a certain time, a white crystalline precipitate began to form in the test tubes and the solution started to turn brown in color. After a predetermined interval of time, the content of each test tube was decomposed by 3 ml. of alcohol, followed by 10 ml. of hydrochloric acid (sp. gr. 1.19), and then poured into a glass flask containing 60 ml. of water. Alcohol addition is recommended for the decomposition procedure on account of the easy solubility of the precipitated complex in alcohol, forming a violet-colored solution. This makes it easy to follow the course of the hydrolysis of the complex. After adding 2-3 drops of methyl orange indicator, the solution is titrated with 0.1*N* solution of KBrO_3 , and the amount of SbCl_3 is calculated for one mole of iso-compound. The amount of SbCl_3 in the original solution must be determined before every experiment, since the SbCl_5 solution changes its factor upon standing and increases its content of SbCl_3 .

The Action of SbCl_5 on *n*-Hexane and Its Isomers

The influence of the solvent on the speed of chlorination: The first experiments were carried out in carbon tetrachloride solution. It was necessary to use very strong solutions of SbCl_5 ; otherwise the chlorination proceeded very slowly. The reaction goes much faster when CHCl_3 is used as solvent. The experimental results are given in Table 1.

Table 1.

Conc. of SbCl_5 Solution	Hydrocarbon	Number of Molecules of SbCl_3 Formed per 1 Molecule of Iso-compound			
		in CCl_4 after —		in CHCl_3 after —	
		1 hour	3 hours	1 hour	3 hours
3 <i>N</i>	2-Methylbutane	0.15	0.40	3.1	3.8
2.25 <i>N</i>	2,3-Dimethylbutane	0.40	0.80
2.25 <i>N</i>	2-Methylpentane	2.5	3.3
2 <i>N</i>	2,3-Dimethylbutane	3.0	3.3
2 <i>N</i>	2-Methylpentane	1.5	1.7	3.3	3.6
1 <i>N</i>	2,3-Dimethylbutane	2.5	2.7
1 <i>N</i>	2-Methylpentane	..	1.0	2.8	3.0

For comparison, we give also the data obtained on isopentane (2-methylbutane). In every experiment, 1 ml. of SbCl_5 solution and 0.1 ml. of 2*N* solution of the iso-compound were used.

Role of SbCl_5 concentration and the degree of chlorination of isomeric hexanes: The experiments were conducted in chloroform solution. Figure 1 shows the influence of SbCl_5 concentration. From this figure, it can be seen that the initial chlorination occurs very rapidly and to an extent which depends upon the concentration of the SbCl_5 solution. Thereafter, the chlorination very suddenly slows down. All the Figure 1

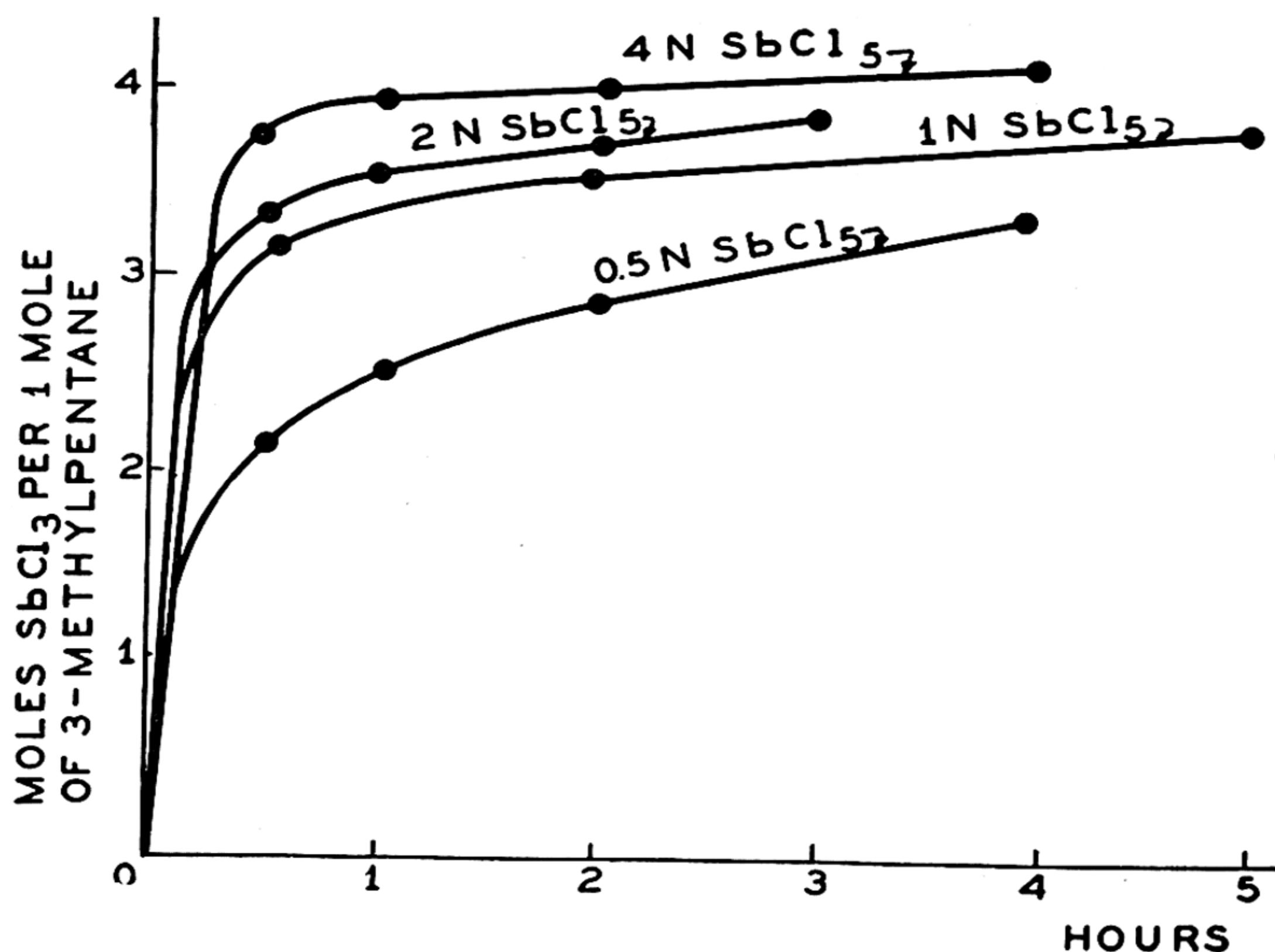


FIG. 1.

experiments were conducted with an excess of SbCl_5 (20 moles per one mole of iso-compound). Special experiments were made to see if *n*-hexane chlorinates in the presence of its isomers. Experiments with 2*N* SbCl_5 solution have shown that hexane itself does not react at room temperature even after 18 hours. With the mixture of isomers, a slight chlorination of *n*-hexane was observed with 1-1.5*N* solutions of SbCl_5 . Experiments were conducted with an even more dilute solution of SbCl_5 (0.5*N*) in order to avoid chlorination of *n*-hexane. In the work with these solutions, it was observed that the reaction does not always begin with the same high velocity, since long standing is necessary in some cases, and even heating does not start the reaction in other examples. After several unsuccessful attempts, it was noticed that moisture has a very substantial influence on the reaction.

Influence of moisture on the activity of SbCl_5 solutions: The chlorination with very dilute solution of SbCl_5 (0.2-0.25*N*), if previously dried over P_2O_5 , occurs without failure and much more energetically than

with former solutions of the same concentration. It is necessary to notice that there is no formation of a precipitate from the P_2O_5 -dried solutions, whereas one is immediately formed from undried solutions. The precipitate obtained on chlorination with $SbCl_5$ is probably a complex (its titration shows that some $SbCl_3$ is present). This complex liquefies in the air and becomes violet-colored in the presence of alcohol or wet ether; an excess of the solvent causes disappearance of the color, due to hydrolysis, and precipitation of antimony acids. In order to study the influence of moisture on the precipitates, a chloroform solution of antimony pentachloride monohydrate ($SbCl_5 \cdot H_2O$) was prepared by adding the corresponding amount of water to $SbCl_5$ with cooling, and dissolving the resulting monohydrate in chloroform. The concentration of this solution was about 1N when saturated at room temperature. It gave voluminous crystalline precipitates on chlorinating 2- and 3-methylpentanes, but 2,3-dimethylbutane did not react. Other experiments with the $SbCl_5 \cdot H_2O$ solution were discontinued. However, detailed study of this complex will be of great interest. The difference between these precipitates obtained from chloroform solution and those described by Schaarschmidt is not clear. It is only necessary to indicate that part of the resulting $SbCl_3$ is always precipitated with the complex in the form of good crystals when working without solvent or with concentrated solutions, as observed in carbon tetrachloride solution in which $SbCl_3$ is very slightly soluble. We found that 22.4 g. of $SbCl_3$ are soluble in 100 ml. of chloroform at room temperature.

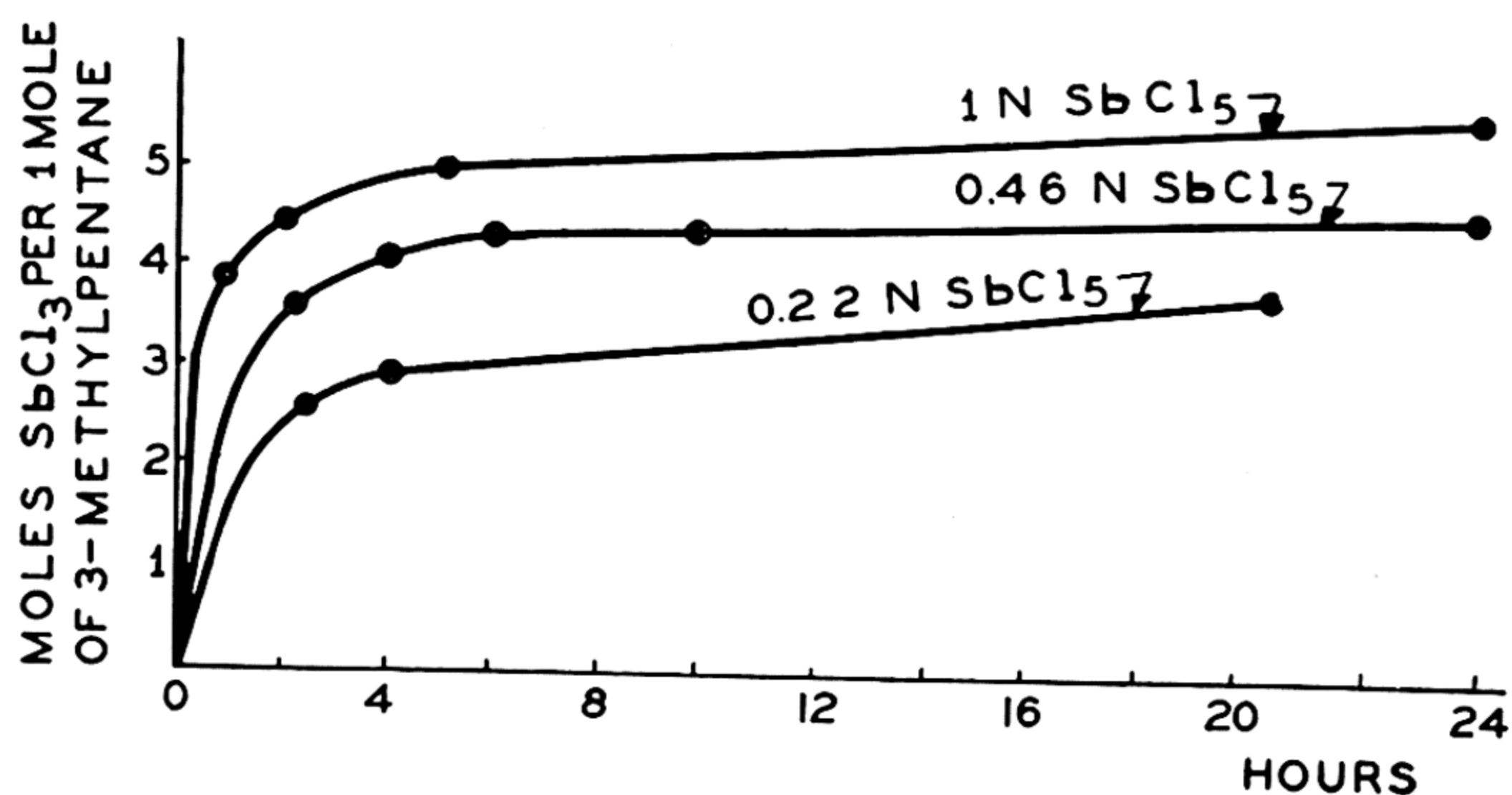


FIG. 2.

Chlorination of hexanes in the presence of P_2O_5 : The absence of precipitation in the reactions using P_2O_5 allowed us to simplify the procedure, since several tests could be conducted from a given vessel. The method will be described at the end of this article. Figure 2 shows the influence of concentration of the $SbCl_5$ solution on the degree of chlorination for 3-methylpentane in the presence of P_2O_5 . All the experi-

ments were carried out with a 12:1 mole relationship of SbCl_5 to hydrocarbon. By comparison with the data presented in Figure 1, it can be seen that SbCl_5 solution dried over P_2O_5 reacts much more energetically. However, the same relationship exists between concentration of SbCl_5 and the degree of chlorination as in the work without P_2O_5 .

Experiments wherein the concentration of both components (iso-compounds and SbCl_5) was varied are considered in Table 2.

Table 2.

Conc. of SbCl_5 Solution	Content of 2-Methylpentane in the Reaction Mixture (%)	Moles of SbCl_5 for 1 Mole of Iso-compound	Number of Moles of SbCl_3 Formed per 1 Mole of 2-Methylpentane during			
			1 hour	2 hours	4 hours	6 hours
0.69 N	0.24	24	4.4	4.9	5.5	..
0.69 N	0.12	48	4.6	5.2	5.8	..
0.69 N	0.06	96	3.7	5.2	6.0	..
0.34 N	0.24	12	3.1	4.0	4.7	..
0.34 N	0.12	24	3.4	4.3	5.0	..
0.34 N	0.06	48	2.4	4.4	5.7	..
0.17 N	0.24	6	1.0	2.0	2.7	3.2
0.17 N	0.12	12	0.3	1.6	2.5	3.6
0.17 N	0.06	24	0.2	0.4	1.5	3.3

The experiments were carried out with solutions of 2-methylpentane and SbCl_5 in CHCl_3 in the presence of P_2O_5 .

The role of iso-hexane structure upon the degree of chlorination is shown in Figure 3. Experiments with 12:1 mole relationship of SbCl_5 to iso-compound were carried out with 0.22N solution of SbCl_5 in CHCl_3

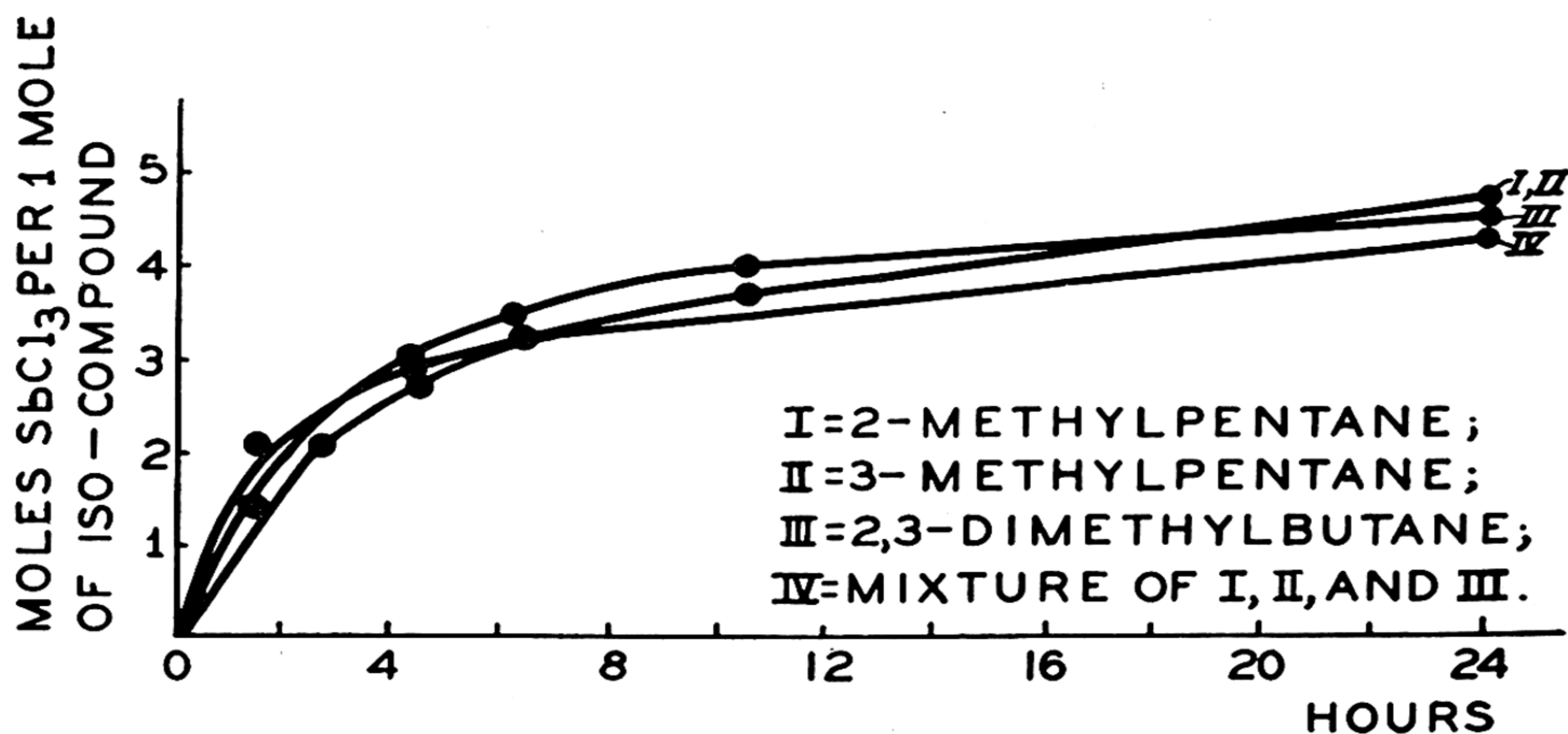


FIG. 3.

in the presence of P_2O_5 . The results were very close, particularly after several hours. Slight differences in the degree of chlorination for the different isomers are due to experimental error, when one takes into consideration that only 15-30 mg. of iso-compound were taken for an experiment. An investigation of the action of SbCl_5 on *n*-hexane in the

presence of P_2O_5 showed that this hydrocarbon is slightly chlorinated, particularly with solutions stronger than $0.5N$ (this depends on the purity of the material used).^{*} However, in the chlorination of hexane and iso-compound mixtures with $SbCl_5$ solutions not exceeding $0.46N$, the degree of chlorination does not exceed the combined amounts of chlorination in the components, as shown in Table 3. It is necessary to remark that,

Table 3.

Time (hrs.)	Number of Moles of $SbCl_3$ Formed per 1 Mole of Hydrocarbon						0.46N Solution of $SbCl_5$	
	0.22N Solution of $SbCl_5$							
	<i>n</i> -Hexane	2-Methyl- pentane	<i>n</i> -Hexane + 6% of 2-Methyl- pentane	2,3-Di- methyl- butane	<i>n</i> -Hexane + 6% of 2,3-Di- methyl- butane		<i>n</i> -Hexane	3-Methyl- pentane
2	0.1	2.1	2.3	2.4	2.4		..	3.4
4	0.15	2.9	3.1	3.0	3.0	0.1	3.8	4.0
6	0.2	3.3	3.5	3.2	3.3	0.2	4.2	4.5
10	0.4	3.7	4.0	3.6	3.7	0.3	4.4	5.0
24	0.5	4.5	5.2	4.3	4.7	0.75	5.1	5.9

in order to have comparable results, the number of $SbCl_5$ molecules taken for hexane chlorination was calculated for the amount of iso-compound contained in the solution. Actually, the consumption of $SbCl_5$ and hexane consists of only a part of the total.

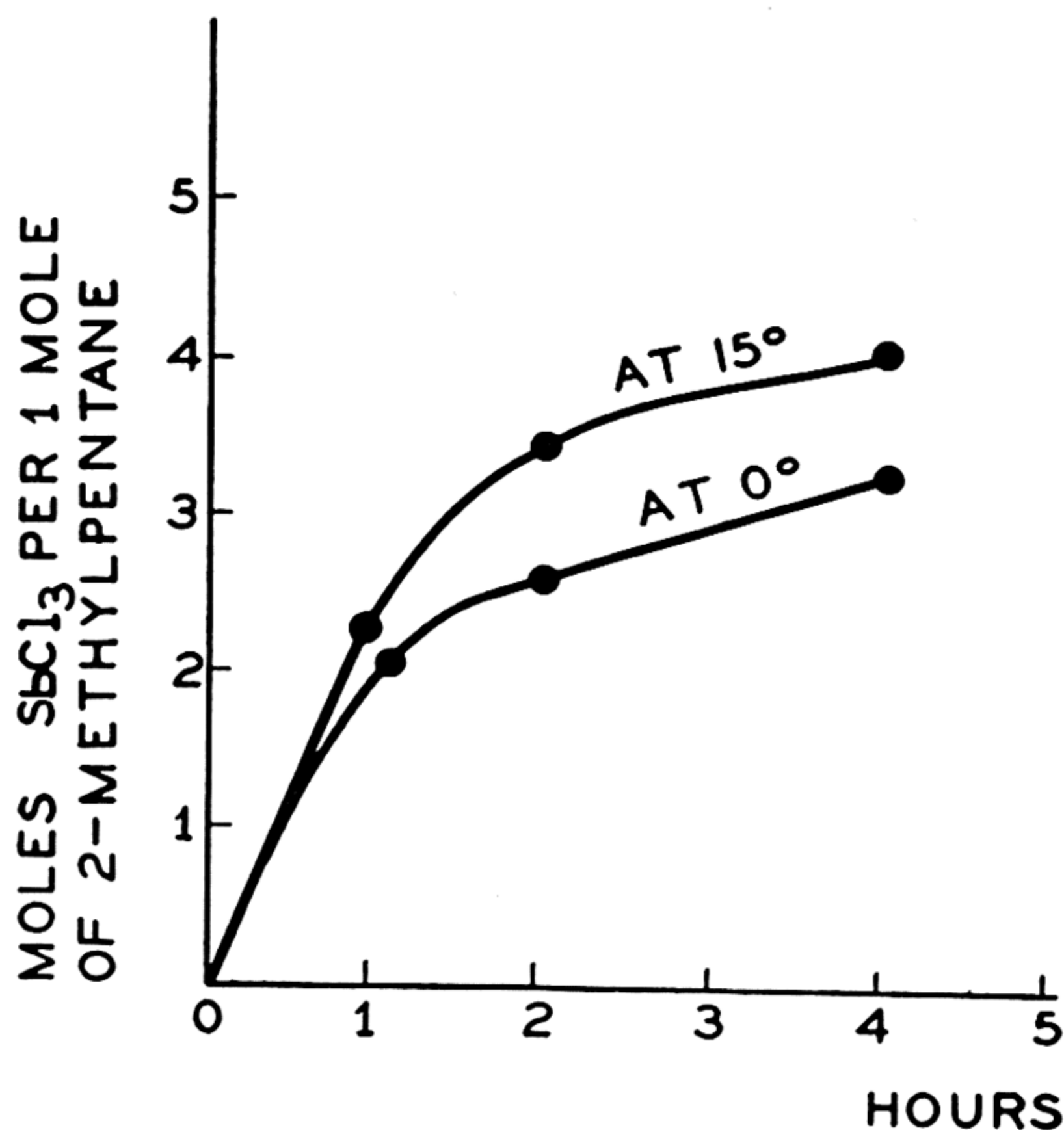


FIG. 4.

^{*} As indicated by Schaarschmidt [*Z. angew. Chem.*, 46, 153 (1933)], the normal hydrocarbons obtained from the hydrocarbon mixtures treated with $SbCl_5$ are less stable to this reagent than the synthetic hydrocarbons. By this we probably can explain the lower stability toward $SbCl_5$ of our synthetic hydrocarbons purified by $SbCl_5$.

Figure 4 shows the influence of temperature on the speed of iso-hexane chlorination. The experiments were carried out at two temperatures with 2-methylpentane and 0.3*N* solution of SbCl_5 in 1:18 molar ratio.

The Action of SbCl_5 on Octane and Its Isomers

The action of SbCl_5 was studied on *n*-octane and two isomers: 4-methylheptane with one tertiary carbon atom and 2,5-dimethylhexane with two tertiary carbon atoms. The experiments on chlorination of 2,5-dimethylhexane and 4-methylheptane showed that these hydrocarbons are chlorinated more slowly than iso-hexanes, as evident from Table 4.

Table 4.

2,5-Dimethyl- hexane	Hydrocarbon Taken, in % of SbCl_5 Solution		Moles of SbCl_5 to 1 Mole of Iso-compound	Number of Moles of SbCl_5 Formed per 1 Mole of Iso-compound during	
	4-Methyl- heptane	2-Methyl- pentane		2 hours	4 hours
0.11	48	2.5	4.1
...	0.11	...	48	2.9	3.9
...	...	0.10	40	4.7	5.1
0.34	15	2.5	4.0
...	0.34	...	15	2.5	3.5

The experiments were carried out with 0.5*N* SbCl_5 at room temperature in the presence of P_2O_5 . As in the case of 2,3-dimethylbutane, the second tertiary carbon atom of 2,5-dimethylhexane had no effect on the speed of chlorination.

Experiments carried out to see if *n*-octane is chlorinated when present alone or with its isomers have showed that pure *n*-octane is not chlorinated under the given conditions. No induced chlorination was observed after addition of iso-octanes (using 0.72*N* SbCl_5) (Table 5).

Table 5.

Time hrs.	Number of Moles of SbCl_5 Formed per 1 Mole of Iso-octane			
	4-Methyl- heptane	0.5 <i>N</i> SbCl_5 <i>n</i> -Octane with 5% of 4-Methylheptane	2,5-Dimethyl- hexane	0.72 <i>N</i> SbCl_5 <i>n</i> -Octane with 7% of 2,5-Dimethylhexane
2	2.9	3.0	4.6	4.6
4	3.8	3.9	5.6	6.0
6	4.2	4.4

The question remains open whether this can be explained by a greater purity of our synthetic octane as compared to hexane or by a greater stability. The experiments were conducted with a 46:1 molar ratio of SbCl_5 to iso-octane. Under the assumption that the other isomeric octanes will behave the same, the results indicate that the method of analysis using SbCl_5 can be used for mixtures of iso-octanes.

Mechanism of chlorination by means of SbCl_5 : From the foregoing statements, it is evident that from 4 to 5 or more moles of SbCl_5 are consumed for 1 mole of iso-compound, depending on the concentration of the reactants. It was impossible to stop the reaction at the first stage of

chlorination when using excess of SbCl_5 . The mechanism of the reactions occurring seems to us to be the following: first, the SbCl_5 reacts with hydrogen of the tertiary carbon atom. The resulting tertiary chloride in the presence of SbCl_5 splits off hydrogen chloride, and chlorine adds to the new double bond with the formation of dichloride. From the latter, hydrogen chloride is split off, chlorine is again added to the double bond, and so on. An analogous mechanism was proposed by A. Kronstein^{323a} to explain bromination of halogen derivatives in the presence of iron. Directive action of iron for bromination at atoms adjacent to those containing halogen was explained by the fact that the iron forms ferric bromide on its surface at the beginning of the reaction, and the scission giving hydrogen bromide is thus catalyzed. An analogous or similar catalytic action must be ascribed to SbCl_5 during chlorination. This substance acts like other metal halides, for instance, in the Friedel-Crafts and other reactions.

A certain energy of activation is necessary for the introduction of the first atom of chlorine, since the chlorination of hydrocarbons is an exothermic reaction. This energy of activation is probably greater than that for the succeeding steps, since chlorination, when once started, does not stop. The reaction is analogous to the oxidation of methane, which is difficult to stop at the intermediary oxidation stage giving formaldehyde. The active molecules of chloride can activate the normal hydrocarbons contained in the mixture and induce the reaction between them and the SbCl_5 . We probably can explain by this fact the induced chlorination of normal hydrocarbons. Stewart and Hanson,^{565a} for instance, observed the same phenomenon during the chlorination of ethylene in the dark in the presence of benzene. The induced reaction, $3\text{Cl}_2 + \text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_6\text{Cl}_6$ occurred, though not by itself in the dark. The authors explained this phenomenon by applying the chain mechanism. It is necessary to note the following also. In our experiments, the degree of chlorination of iso-compounds was calculated from the total expenditure or use of SbCl_5 . Whether or not a part of the iso-structure hydrocarbon remains unattacked, or whether all the molecules are equally chlorinated, and the dependence of these upon the process conditions, are still unsolved. Several experiments on chlorination of chlorides were carried out in

Table 6.

Halogen Derivative	Experiment Time (hrs.)	Moles of SbCl_3 Formed per 1 Mole of Chloride
Propyl Chloride	2	0
2-Chloro-2-methylbutane	0.5	0.96
2-Chloro-2-methylbutane	2	1.05
2-Chloro-2-methylbutane + Propyl Chloride (1:1)	2	0.95 ^a
2-Chloro-2-methylpropane	2	0.98

^a Calculated on tertiary chloride.

order to prove our ideas on the mechanism of chlorination. These experiments were conducted under the conditions mentioned in the beginning of this article, *i.e.*, 0.1*N* SbCl₅ in CCl₄ at 0°, and are presented in Table 6.

From the table, it is evident that tertiary chlorides react even with a 0.1*N* solution of SbCl₅ in CCl₄. The reaction ends at the disubstituted stage, but the chlorination of iso-structure hydrocarbons, as already shown, requires 2-2.5*N* solution of SbCl₅ in CCl₄ (without P₂O₅). As expected, the action of a 2*N* solution of SbCl₅ in chloroform on the tertiary chlorides does not stop at monochlorination but continues to 3 or 4 molecules, as in the case of hydrocarbons. The experiments demonstrate the greater ease of the second stage of chlorination that is connected with HCl evolution and the addition of chlorine at the double bond. We did not continue the study of the action of SbCl₅ on chloro-derivatives; however, a detailed study would be of great value for the development of an analytical method for tertiary chlorides.

Summarizing the foregoing statements, it is an obvious conclusion that the complex action of SbCl₅ on hydrocarbons does not permit us to apply a definite kinetic equation to the process. However, sufficient data have been obtained to develop a practical method for the analysis of mixtures of isomeric hexanes or octanes. An independence of chlorination speed and iso-compound structure (for iso-hexanes and iso-octanes among themselves) allows us to compare the degree of chlorination in unknown mixtures with that of a control hydrocarbon. A description of a practical method follows.

Method of Analysis of *n*-Hexane and Octane in Mixtures Containing their Isomers

A 0.5*N* solution of antimony pentachloride in chloroform is first prepared. The chloroform for this purpose is washed by sulfuric acid, sodium carbonate, and water, dried, and distilled. It is then dried by P₂O₅.^{*} The purified chloroform is introduced into a ground, glass-stoppered flask, and the required amount of 0.4-0.6*N* solution of SbCl₅ is added. Next, P₂O₅ is inserted. The solution is shaken for 0.5 to one hour, after which it is allowed to settle until all the P₂O₅ has deposited as a compact layer at the bottom, with a clear solution of SbCl₅ above. From two to three ml. of this solution are titrated to determine the amount of SbCl₅ and SbCl₃. If necessary, the solution is concentrated by SbCl₅ addition or diluted with the foregoing chloroform. The determination of iso-compounds is conducted as follows: 0.25 ml. of some iso-compound in octane or hexane containing a definite concentration (5-10%) is added to a graduated cylinder (I) of 25 ml. capacity; 0.5

^{*} This purification is recommended, otherwise the SbCl₅ solution changes its factor.

ml. of the solution to be investigated is introduced into a cylinder (II) of the same capacity. If the specific gravity is unknown, one can measure the investigated materials by weight in sealed glass ampoules instead of micropipetting. Both cylinders are filled to the mark (15-25 ml., depending on the expected amount of isomers) with SbCl_5 solution, and a small quantity of P_2O_5 is added to each. The cylinders are shaken and then left alone. After several minutes the reaction starts; this may be noticed by the color change. The solution, which was originally light yellow, becomes gradually red and then dark brown. Sometimes, the reaction does not start immediately, but the solution is usually dark at the end of the first hour. After 2-3 and 4-6 hours, 3 ml. of solution are pipetted from each cylinder and titrated for SbCl_3 content by means of 0.1N KBrO_3 solution, as previously indicated. The pipette must be protected by a calcium chloride tube to avoid introduction of moisture into the cylinder during withdrawal of the sample. Since only a few ml. of solution are necessary for the titration, we used a 10 ml. burette with 1/20 ml. divisions. A parallel determination of SbCl_3 is made on a 3 ml. sample of the original solution of SbCl_5 in chloroform, and the amount thereof is used as a correction for the titrations.

It is possible to calculate the weight per cent of iso-compound within the unknown sample by comparing the titration results for the cylinder II sample with those for cylinder I during the same time of chlorination, according to the following formula,

$$x = \frac{a \cdot c \cdot e \cdot f}{b \cdot d \cdot g}$$

where a is the number of ml. of 0.1N KBrO_3 that was used for the titration of 3 ml. from cylinder II; b is the number of ml. of 0.1N KBrO_3 solution that was used for the titration of 3 ml. of solution from control cylinder I; c is the number of ml. of SbCl_5 solution placed in cylinder II; d is the number of ml. of SbCl_5 solution placed in cylinder I; e is the weight per cent of iso-compound in the hexane-octane control solution for cylinder I; f is the number of ml. of the control solution; and g is the number of ml. of the unknown solution being analyzed. The results obtained for 2-3 and 4-6 hours usually differ very little. However, in certain cases where the beginning of the reaction proceeds slowly (at low concentration of iso-compound), the results are more accurate after 4-6 hours, since the difference in velocity of chlorination is thereby compensated. Tests of longer duration are not advisable, because the chlorination velocity becomes very slow. It is possible for the initial molar ratio of SbCl_5 to iso-compound to be less than 12:1 whenever the content of iso-compounds is large. The amount of unused SbCl_5 must be calculated after the analysis,

since it is not recommended to work below this limit. If less than 6-7:1 molar ratio prevailed, the analysis must be repeated and the amount of hexane or octane decreased to 0.2-0.3 ml.

Finally, we present in Table 7 the results of analyses for several control mixtures containing isomers within *n*-hexane and octane. These

Table 7.

Expt. No.	Mixture Taken for the Analysis			Control Solution	Indicated Percentage of Iso-compound			
					2 hrs.	3 hrs.	4 hrs.	6 hrs.
1	5% 2,5-Dimethylhexane 5% 4-Methylheptane	} in 0.5 ml. of <i>n</i> -Octane		5% 4-Methylheptane in 0.5 ml. of <i>n</i> -octane	11.6	...	11.9	...
2	12.5% 2,5-Dimethylhexane 12.5% 4-Methylheptane			5% 4-Methylheptane in 0.5 ml. of <i>n</i> -octane	28.3	...	28.0	...
3	10% 2,5-Dimethylhexane 10.8% 4-Methylheptane	} in 0.6 ml. of <i>n</i> -Octane		5% 2,5-Dimethylhexane in 0.6 ml. of <i>n</i> -Octane	...	18.6	...	21.4
4	4.8% 2,3-Dimethylbutane 4.5% 2-Methylpentane			5.5% 2-Methylpentane in 0.5 ml. of Hexane	...	9.0	...	8.8
5	10% 2,3-Dimethylbutane 10.5% 2-Methylpentane	} in 0.5 ml. of <i>n</i> -Hexane		5.5% 2-Methylpentane in 0.5 ml. of Hexane	...	19.7	...	19.5
6	4.5% 2,3-Dimethylbutane 4.5% 4-Methylheptane			Control Solution #4	...	9.5	...	9.2
				Control Solution #1	...	7.8	...	8.0

analyses were conducted according to the method described. From this table, it can be seen that the results were very close, particularly if the small amount of iso-compound used in the analysis is taken into consideration. A mixture of an iso-hexane and an iso-octane was used in experiment 6. The results of its analysis were calculated by using iso-octane and also iso-hexane (as the basis of control), as can be seen from Table 7. Even in such cases, the results were satisfactory. We suggest the future extension of this method's utility to the study of different mixtures of hydrocarbons containing a tertiary carbon atom, because this problem has exceptional importance in the study of motor fuels. We can mention that preliminary chlorination experiments on cyclohexane in its mixture containing methylcyclohexane showed a complete possibility of quantitative determination.

Conclusions

1. Chlorination of isomeric hexanes and octanes was studied quantitatively by determination of SbCl_5 expenditure.

2. Compounds containing hydrogen on a tertiary carbon atom are readily chlorinated by dilute SbCl_5 solutions.

Appendix II

The following translation of O. W. Bauer's Thesis, Eidgenössischen Technischen Hochschule, Zürich, pp. 54-60 (1940), covers some fundamental work on iso-alkane determination. It is submitted for the perusal of readers interested in the quantitative estimation of alkane isomers by means of physical methods based on "additive functions."

Determination of the Number of Side-Chains in Alkanes by Means of the Parachor

Marder in an extensive article ^{358a} discusses the application of physical constants to the study of motor fuel composition. In the following article we will discuss the use of the parachor in analysis of hydrocarbons.

Sugden ^{574c} suggested an expression, called parachor, which is a constant, independent of temperature, for every pure chemical compound:

$$P = s^{1/4} \cdot \frac{M}{D}$$

P = Molecular parachor
 s = Surface tension at the temperature t°
 M = Molecular weight
 D = Density of the compound in the liquid phase at the temperature t°

The advantage of the parachor is its additive property which, as with molecular refraction, permits it to be calculated from atomic contributions. These atomic contributions are called increments and are determined empirically. Values calculated from them check well with those determined by the above formula.

As can be seen, the molecular parachor strongly depends on molecular weight. Since hydrocarbon mixtures nearly always contain compounds with different molecular weights, it is advantageous to use the specific parachor, which is the parachor value for 1 gram of substance:

$$p = \frac{1}{D - \frac{M}{24055}} \cdot s^{1/4}$$

The molecular parachors and specific parachors decrease in the following sequence: alkanes, alkenes, naphthenes, and aromatics. The analytical method of Marder for determination of these hydrocarbon classes is based on this property. Since the present work concerns only alkanes, we shall continue with a discussion of the differences in alkane parachors.

When the parachors of alkanes are calculated from the increments, there is no difference between normal and iso-alkane values. However, when the parachor is determined from the physical constants for various isomers of a certain alkane, there is a remarkable deviation from the theoretical value. This deviation increases with the number of side-chains. Both parachors, P and p , decrease with increasing branching. The decrease in molecular parachor averages about 2.5 per side-chain. This requires that the increments assume different values for secondary, tertiary, and quaternary carbon atoms.

From the parachor measurement for an alkane mixture, it is possible to determine the average degree of branching of the alkanes, provided no other classes of hydrocarbons are present. The molecular parachor increases with increase in molecular weight and decreases with increase in branching. The specific parachor, on the contrary, decreases with increase in molecular weight and with increase in branching.

A determination can be conducted in the following manner: First, curves of parachors *versus* molecular weight are constructed for normal, monosubstituted, disubstituted, and higher-substituted alkanes. Then the unknown mixture of alkanes is carefully separated into fractions of the same molecular weight, and physical measurements are made on these fractions. The degree of branching in the unknown mixture is obtained by a comparison of the results of these measurements with the curves. The original literature must be consulted for a detailed discussion of the theory of the parachor.^{358a, 574c}

Procedure of Measurement

The density and surface tension of the investigated alkanes must be measured in order to determine the specific parachor. The density is measured by means of a picnometer with ground glass cap and thermometer and of 10 cc. capacity. For the surface tension measurement, Marder suggests the capillary rise apparatus of Ubbelohde^{600b} as a very accurate one. However, the maximum bubble pressure method of Sugden^{574a, 574b} was tried first.

The principle of this method consists of the following: two glass tubes of different diameters are placed in the liquid to be investigated and air is drawn through them. The pressure difference upon suction through the two tubes is a measure of the surface tension. The original literature^{574a, 574b} must be consulted on account of the somewhat complicated theoretical basis of this method. The surface tension is calculated by means of the following formula:

$$s = A \cdot P \left(1 + 0.69 r_2 \cdot \frac{gD}{P} \right)$$

- s = Surface tension at the temperature t°
 A = Previously determined constant for the apparatus
 P = Observed pressure difference (height \times density of the liquid
 \times acceleration of gravity)
 r_2 = Radius of the wider tube
 g = Acceleration of gravity
 D = Density of the liquid at the temperature t°

In order that the calculation may require the diameter of only the wider tube, the other tube is selected as narrow as possible, that is to say, a capillary is used. The diameter, r_2 , of the wider tube is measured very carefully with the aid of a magnifying glass. The pressure, P , is measured by means of a U-tube containing an indicating liquid. It is immaterial what kind of manometer fluid is used, provided that its density is known. Distilled water, colored red by a drop of acid and methyl orange, was used. Its density was taken as that of distilled water. The suction required to pull air through the tubes was obtained by attaching a dropping funnel filled with mercury to the apparatus. The velocity of air suction was controlled by regulating the speed of mercury withdrawal. The entire arrangement consists, therefore, of a measuring apparatus with two tubes, the dropping funnel with mercury, and the manometer (U-tube). The required quantity of hydrocarbon liquid was 1.5 to 2 cc. [For a description of the apparatus, etc., see S. Sugden, *J. Chem. Soc.* 121, 858-866 (1922); 125, 27-31, 1177-1189 (1924)].

Before proceeding with an actual measurement, the apparatus constant, A , must be determined. Benzene was used for this purpose because its surface tension and density are well known. The benzene must be chemically pure, which means thiophene-free but not absolutely free of water, since traces of moisture do not affect the surface tension of benzene. One could determine the apparatus constant also with pure distilled water. However, this is not advisable, since the surface tension of water differs too much from that of hydrocarbons.

During the measurement, the apparatus must be kept at constant temperature. Since most of the measurements were conducted at room temperatures, it was sufficient to use a beaker with water or paraffin oil, as the thermostat.

The disadvantage of Sugden's method consists of a partial evaporation of the liquid and its gradual change in composition caused by the passage of air. However, taking into consideration that the differences in the vapor pressure of isomers are very small and that the experiment is carried out in a very short time, the changes in composition cannot be excessive.

The other method of determining the surface tension is the capillary rise method of Ubbelohde.^{600b} Here, also, the extensive theoretical basis cannot be given, and the original literature must be consulted.

The arrangement is somewhat simpler than Sugden's. The apparatus consists of two tubes and a capillary, which are sealed parallel to each other onto a small vessel. The capillary is calibrated and represents the most important part of the apparatus. The following procedure is used: The liquid is introduced into the widest tube up to the mark and the whole apparatus placed in a thermostat consisting of a beaker filled with water or paraffin oil. After the liquid attains the temperature of the thermostat, it is forced high into the capillary by means of a rubber bulb, so that a little liquid flows out. The pressure is then released, whereupon the liquid will settle in the capillary at different heights, depending on its surface tension. The height is measured, as in Sugden's method, by means of a cathetometer within an accuracy of ± 0.05 mm.

This apparatus also must be standardized. A calibration of the capillary is required. The standardization is again carried out with benzene. The surface tension is calculated by means of the following formula:

$$s = h \cdot D \cdot \frac{s_B}{h_B \cdot D_B}$$

- s = The observed surface tension at the temperature t°
- h = Capillary rise of the observed liquid at the temperature t°
- D = Density of the observed liquid at the temperature t°
- s_B = Surface tension of benzene at the temperature t_1°
- h_B = Capillary rise of benzene at the temperature t_1°
- D_B = Density of benzene at the temperature t_1°

For the ensuing work, we used a standardized apparatus that was kindly loaned by the "Institute for Brown Coal and Mineral Oil Research" of the Berlin Technischen Hochschule. The calculation followed the formula:

$$s = h \cdot D \cdot k, \text{ whereby } k = \frac{s_B}{h_B \cdot D_B}$$

It was necessary to add 0.280 to the observed height for the uncalibrated part.

The following tables represent the results of a standardization of Sugden's apparatus and of measurements on *n*-octane, 2-methylheptane, and their mixtures.

Table 1. Determination of the Apparatus Constant A .
$$A = \frac{s}{P \left(1 + 0.69 r_2 \cdot \frac{gD}{P} \right)}$$

Expt. No.	Height (cm.)	Temp. (°C.)	Density of Benzene, D_4^t	Surface Tension of Benzene s_t	Apparatus Constant, A
83	9.19	16.0	0.8830	29.40	0.003115
84	0.03	20.0	0.8791	28.85	0.003114
85	8.93	22.0	0.8769	28.59	0.003115
86	8.89	23.0	0.8760	28.46	0.003114
87	8.80	25.0	0.8738	28.23	0.003123
88	8.75	26.0	0.8727	28.10	0.003119
89	8.67	28.0	0.8704	27.84	0.003118
Average					0.003117

The average value was 0.003117. It was used in the following measurements of parachor.

Table 2. Determination of the Parachors of Various Octanes.
Determination of the Surface Tension and Parachor of n -Octane

Expt. No.	Temp. (°C.)	Density D_4^t	Height (cm.)	Surface Tension	Molecular Parachor, P	Specific Parachor, p
90	22.0	0.7007	6.805	20.75	349.9	3.066
91	24.0	0.6991	6.705	20.54	349.8	3.065
92	25.0	0.6983	6.69	20.49	350.0	3.067
93	28.0	0.6958	6.61	20.10	349.5	3.063
Average					349.8	3.065

Averaging of the parachor measurements for n -octane gave:

Molecular parachor	349.8
Specific parachor	3.065

Determination of the Surface Tension and Parachor of 2-Methylheptane

Expt. No.	Temp. (°C.)	Density D_4^t	Height (cm.)	Surface Tension	Molecular Parachor, P	Specific Parachor, p
94	14.6	0.7038	6.72	20.58	347.7	3.047
95	21.4	0.6982	6.52	19.98	347.7	3.047
96	22.6	0.6973	6.475	19.86	347.7	3.047
97	24.8	0.6955	6.405	19.63	347.7	3.047
98	30.0	0.6913	6.245	19.10	347.3	3.043
Average					347.7	3.047

Averaging of the parachor measurements for 2-methylheptane gave:

Molecular parachor	347.7
Specific parachor	3.047

Determination of the Surface Tension and Parachor of 2,2,4-Trimethylpentane

Expt. No.	Temp. (°C.)	Density D_4^t	Height (cm.)	Surface Tension	Molecular Parachor, P	Specific Parachor, p
99	10.8	0.6983	6.205	19.05	343.9	3.013
100	17.0	0.6934	6.04	18.53	343.9	3.013
101	22.0	0.6895	5.90	18.09	343.8	3.011
102	24.6	0.6875	5.82	17.80	343.4	3.009
Average					343.7	3.012

Averaging of the parachor measurements for 2,2,4-trimethylpentane gave:

Molecular parachor	343.7
Specific parachor	3.012

[illegible]

Model	Specificity	Parachor	Model	Specificity	Parachor	Model	Specificity	Parachor
MolVec	0.95	0.95	MolVec	0.95	0.95	MolVec	0.95	0.95
Specific	0.95	0.95	Specific	0.95	0.95	Specific	0.95	0.95

1. **Introduction**
 2. **Background**
 3. **Methodology**
 4. **Results**
 5. **Discussion**
 6. **Conclusion**
 7. **References**
 8. **Appendix**
 9. **Index**
 10. **Table of Contents**
 11. **Abstract**
 12. **Summary**
 13. **Key Words**
 14. **Keywords**
 15. **Subject Headings**
 16. **Classification**
 17. **Indexing**
 18. **Keywords**
 19. **Subject Headings**
 20. **Classification**
 21. **Indexing**
 22. **Keywords**
 23. **Subject Headings**
 24. **Classification**
 25. **Indexing**
 26. **Keywords**
 27. **Subject Headings**
 28. **Classification**
 29. **Indexing**
 30. **Keywords**
 31. **Subject Headings**
 32. **Classification**
 33. **Indexing**
 34. **Keywords**
 35. **Subject Headings**
 36. **Classification**
 37. **Indexing**
 38. **Keywords**
 39. **Subject Headings**
 40. **Classification**
 41. **Indexing**
 42. **Keywords**
 43. **Subject Headings**
 44. **Classification**
 45. **Indexing**
 46. **Keywords**
 47. **Subject Headings**
 48. **Classification**
 49. **Indexing**
 50. **Keywords**
 51. **Subject Headings**
 52. **Classification**
 53. **Indexing**
 54. **Keywords**
 55. **Subject Headings**
 56. **Classification**
 57. **Indexing**
 58. **Keywords**
 59. **Subject Headings**
 60. **Classification**
 61. **Indexing**
 62. **Keywords**
 63. **Subject Headings**
 64. **Classification**
 65. **Indexing**
 66. **Keywords**
 67. **Subject Headings**
 68. **Classification**
 69. **Indexing**
 70. **Keywords**
 71. **Subject Headings**
 72. **Classification**
 73. **Indexing**
 74. **Keywords**
 75. **Subject Headings**
 76. **Classification**
 77. **Indexing**
 78. **Keywords**
 79. **Subject Headings**
 80. **Classification**
 81. **Indexing**
 82. **Keywords**
 83. **Subject Headings**
 84. **Classification**
 85. **Indexing**
 86. **Keywords**
 87. **Subject Headings**
 88. **Classification**
 89. **Indexing**
 90. **Keywords**
 91. **Subject Headings**
 92. **Classification**
 93. **Indexing**
 94. **Keywords**
 95. **Subject Headings**
 96. **Classification**
 97. **Indexing**
 98. **Keywords**
 99. **Subject Headings**
 100. **Classification**
 101. **Indexing**
 102. **Keywords**
 103. **Subject Headings**
 104. **Classification**
 105. **Indexing**
 106. **Keywords**
 107. **Subject Headings**
 108. **Classification**
 109. **Indexing**
 110. **Keywords**
 111. **Subject Headings**
 112. **Classification**
 113. **Indexing**
 114. **Keywords**
 115. **Subject Headings**
 116. **Classification**
 117. **Indexing**
 118. **Keywords**
 119. **Subject Headings**
 120. **Classification**
 121. **Indexing**
 122. **Keywords**
 123. **Subject Headings**
 124. **Classification**
 125. **Indexing**
 126. **Keywords**
 127. **Subject Headings**
 128. **Classification**
 129. **Indexing**
 130. **Keywords**
 131. **Subject Headings**
 132. **Classification**
 133. **Indexing**
 134. **Keywords**
 135. **Subject Headings**
 136. **Classification**
 137. **Indexing**
 138. **Keywords**
 139. **Subject Headings**
 140. **Classification**
 141. **Indexing**
 142. **Keywords**
 143. **Subject Headings**
 144. **Classification**
 145. **Indexing**
 146. **Keywords**
 147. **Subject Headings**
 148. **Classification**
 149. **Indexing**
 150. **Keywords**
 151. **Subject Headings**
 152. **Classification**
 153. **Indexing**
 154. **Keywords**
 155. **Subject Headings**
 156. **Classification**
 157. **Indexing**
 158. **Keywords**
 159. **Subject Headings**
 160. **Classification**
 161. **Indexing**
 162. **Keywords**
 163. **Subject Headings**
 164. **Classification**
 165. **Indexing**
 166. **Keywords**
 167. **Subject Headings**
 168. **Classification**
 169. **Indexing**
 170. **Keywords**
 171. **Subject Headings**
 172. **Classification**
 173. **Indexing**
 174. **Keywords**
 175. **Subject Headings**
 176. **Classification**
 177. **Indexing**
 178. **Keywords**
 179. **Subject Headings**
 180. **Classification**
 181. **Indexing**
 182. **Keywords**
 183. **Subject Headings**
 184. **Classification**
 185. **Indexing**
 186. **Keywords**
 187. **Subject Headings**
 188. **Classification**
 189. **Indexing**
 190. **Keywords**
 191. **Subject Headings**
 192. **Classification**
 193. **Indexing**
 194. **Keywords**
 195. **Subject Headings**
 196. **Classification**
 197. **Indexing**
 198. **Keywords**
 199. **Subject Headings**
 200. **Classification**
 201. **Indexing**
 202. **Keywords**
 203. **Subject Headings**
 204. **Classification**
 205. **Indexing**
 206. **Keywords**
 207. **Subject Headings**
 208. **Classification**
 209. **Indexing**
 210. **Keywords**
 211. **Subject Headings**
 212. **Classification**
 213. **Indexing**
 214. **Keywords**
 215. **Subject Headings**
 216. **Classification**
 217. **Indexing**
 218. **Keywords**
 219. **Subject Headings**
 220. **Classification**
 221. **Indexing**
 222. **Keywords**
 223. **Subject Headings**
 224. **Classification**
 225. **Indexing**
 226. **Keywords**
 227. **Subject Headings**
 228. **Classification**
 229. **Indexing**
 230. **Keywords**
 231. **Subject Headings**
 232. **Classification**
 233. **Indexing**
 234. **Keywords**
 235. **Subject Headings**
 236. **Classification**
 237. **Indexing**
 238. **Keywords**
 239. **Subject Headings**
 240. **Classification**
 241. **Indexing**
 242. **Keywords**
 243. **Subject Headings**
 244. **Classification**
 245. **Indexing**
 246. **Keywords**
 247. **Subject Headings**
 248. **Classification**
 249. **Indexing**
 250. **Keywords**
 251. **Subject Headings**

Appendix III

Since the main part of this monograph was written, new material has appeared which was thought highly desirable for incorporation as a supplement in the interest of bringing the data up to February 1, 1942.

The importance of the isomerization of normal butane, pentane, hexane, and naphtha in the production of 100 octane gasoline, which makes possible the tremendous speeds and load-carrying capacities of today's airplanes, is indeed great. Furthermore, the isomerization of normal butane into isobutane, followed by dehydrogenation to isobutene, supplies a base material for polymerization in "butyl rubber" production.

In the United States, South America, and the Near East, isomerization plants are under commercial construction or operation [Anon., *Refiner Natural Gasoline Mfr.*, 21, 103 (1942)]. These plants produce isobutane from *n*-butane for the synthesis of 2,2,4-trimethylpentane or can isomerize "ordinary gasoline" into aviation gasoline or its components. They are obviously opening new fields for the use of natural, casinghead, and straight-run gasolines, which are readily isomerizable into branched-chain hydrocarbons of more appropriate octane rating and combustion properties. These trends call for latest data on both pure and applied isomerizations.

PURE ISOMERIZATION

Heats of combustion of simple aliphatic and cyclic hydrocarbons at constant pressure have been investigated by V. P. Golmov [*J. Gen. Chem. (U.S.S.R.)*, 11, 405-410 (1941)].* Hydrogen atoms attached to primary, secondary, and tertiary carbon atoms were given increasing thermochemical values of 30.7, 31.4, and 31.7 kilocalories per gram-atomic weight, respectively. The excess of energy in cyclic hydrocarbons as compared with their aliphatic isomers was also considered. Since this article is concerned with the calculation of theoretical values of heats of combustion, its scope can be readily extended to yield theoretical values of heats of isomerization.

Heat capacity data for gaseous 2,2,4-trimethylpentane at 150-185° and zero or atmospheric constant pressure have been published by M. Kiperash and G. S. Parks [*J. Am. Chem. Soc.*, 64, 179 (1942)]. The consistency of the observed data and corresponding values calculated

* A complete translation by J. G. Tolpin appears in Universal Oil Products Company Survey of Foreign Petroleum Literature, September 5, 1941.

from the statistical equation of K. S. Pitzer [*J. Am. Chem. Soc.*, **62**, 1224-1227 (1940)], is considered as reasonable, the deviations being around 1.5 per cent. The foregoing data are part of a soundly based "thermodynamics of isomerization."

Heats of formation and of combustion for the 9 isomeric heptanes in the liquid state at 25° and atmospheric pressure have been reported by G. F. Davies and E. C. Gilbert [*J. Am. Chem. Soc.*, **63**, 2730-2732 (1941)]. The exothermic heats of isomerization of *n*-heptane into 2-methylhexane, 3-methylhexane, 3-ethylpentane, 2,2-dimethylpentane, 2,3-dimethylpentane, 2,4-dimethylpentane, 3,3-dimethylpentane, and 2,2,3-trimethylbutane for these conditions of state were obtained directly from the heats of combustion and reported as 1.25, 0.52, 0.19, 3.91, 1.70, 2.985, 3.025, and 2.80 kilocalories per gram-mole, respectively. Heats of isomerization of *n*-heptane into its 8 isomers have been determined also by E. J. R. Prosen and F. D. Rossini [*J. Research Natl. Bur. Standards*, **27**, 519-528 (1941) (Research Paper No. 1439)]. Their values for the liquid state at 25° and atmospheric pressure are in substantial accordance with those of Davies and Gilbert, being 1.30 ± 0.25 , 0.72 ± 0.25 , 0.14 ± 0.23 , 3.42 ± 0.28 , 2.18 ± 0.26 , 2.54 ± 0.16 , 2.44 ± 0.15 , and 3.00 ± 0.22 kilocalories per gram-mole for the given order of branched heptanes. The corresponding values for the ideal gaseous state at 25° C. were reported by Prosen and Rossini as 1.80 ± 0.29 , 1.18 ± 0.29 , 0.52 ± 0.27 , 4.45 ± 0.32 , 2.80 ± 0.30 , 3.40 ± 0.22 , 3.24 ± 0.21 , and 4.17 ± 0.27 kilocalories per gram-mole, respectively. For the exothermic heats of isomerization of *n*-octane into 2-methylheptane and 3-methylheptane in the liquid state at 25° and atmospheric pressure, the latter investigators cite unpublished values of 1.50 ± 0.30 and 0.63 ± 0.30 kilocalories per gram-mole, respectively.

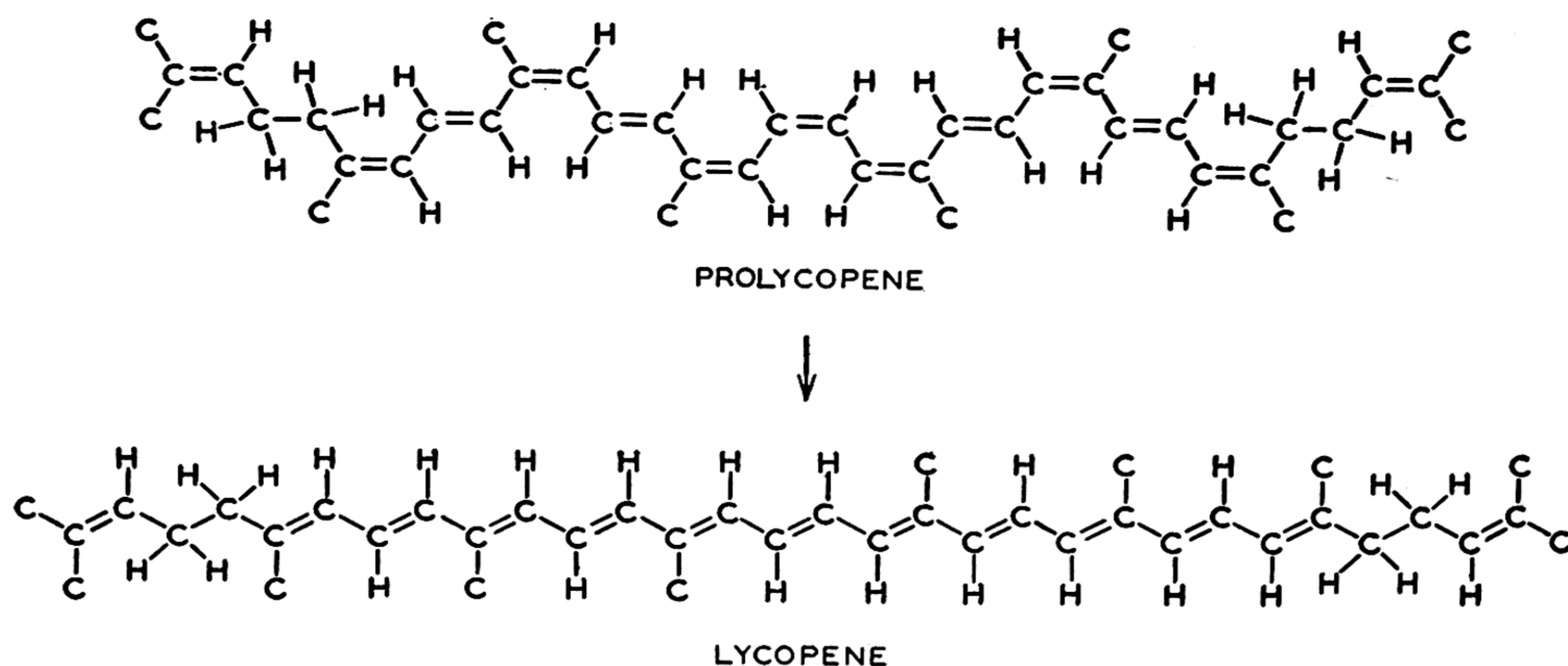
The isomerization of *n*-butane at 120° in the presence of one-fifth its weight of aluminum chloride and some water yielded upwards of 50 per cent of isobutane for a contact time of 30 minutes, according to O. Ferrari [*Rev. facultad cienc. quim. (Univ. nacl. La Plata)*, **15**, 297-305 (1940); *Chem. Abs.*, **35**, 7365 (1941)].

A short review on "Isomerization of Unsaturated Hydrocarbons," including several related reactions of hydrocarbons, alcohols, and carboxylic acids, has been published by E. Bergmann [*Chem. Rev.*, **29**, 529-551 (1941)].

The work of R. H. Ewell and P. E. Hardy on "Isomerization Equilibrium among the Branched Chain Pentenes," which was presented as a Petroleum Division Paper at the Atlantic City Meeting of the American Chemical Society, has been revised and published [*J. Am. Chem. Soc.*, **63**, 3460-3465 (1941)]. It should be read by those interested in isomerization of either straight or branched-chain pentenes, in provisional values

of the absolute entropies of the latter pentenes, or in their entropies of isomerization.

6,7-10,11-14,15-16,17-18,19-22,23-26,27-*cis*-8,9-12,13-20,21-24,25-*trans*-2,6,10,14,19,23,27,31-Octamethyldotriacontatriecaene - 2,6,8,10,12,14,16,18,20,22,24,26,30 is the structure assigned to prolycopene, the principal pigment of ripe tangerine tomato fruits, by L. Zechmeister, A. L. LeRosen, F. W. Went, and L. Pauling [*Proc. Nat. Acad. Sci. U. S.*, 27, 468-474 (1941)]. These investigators have found that a solution of prolycopene in petroleum ether upon contact with iodine dissolved in the same solvent forms lycopene and neolycopene within two seconds. Lycopene is the main component of the resulting isomeric mixture and is believed to have the completely *trans* structure of 6,7-8,9-10,11-12,13-14,15-16,17-18,19-20,21-22,23-24,25-26,27-*trans*-2,6,10,14,19,23,27,31-octamethyldotriacontatriecaene-2,6,8,10,12,14,16,18,20,22,24,26,30. This assignment corresponds to less overlapping of hydrogen atoms and methyl groups than is probably present in the highly *cis*-structured prolycopene and in several "bond planar" intermediates advanced mainly on mathematical grounds.



The methylcyclopentane and cyclohexane equilibrium has been investigated with the aid of Raman spectra measurements by S. Mizusima, Y. Morino, and R. Huzisiro [*J. Chem. Soc. Japan*, 62, 587-591 (1941); *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, 38, No. 1034, 401-408 (1941) (in English)]. Aluminum chloride with water was used to convert the cyclohexane into equilibrium mixtures containing 12.6 per cent of methylcyclopentane at 30° or 26.5 per cent at 78.5°. The corresponding entropy change at 25° was calculated to be 9.2 ± 1.2 entropy units.

Two instances of the formation of spiro[4.5]decenes by cyclization in the presence of sulfuric acid of 84 per cent concentration have been

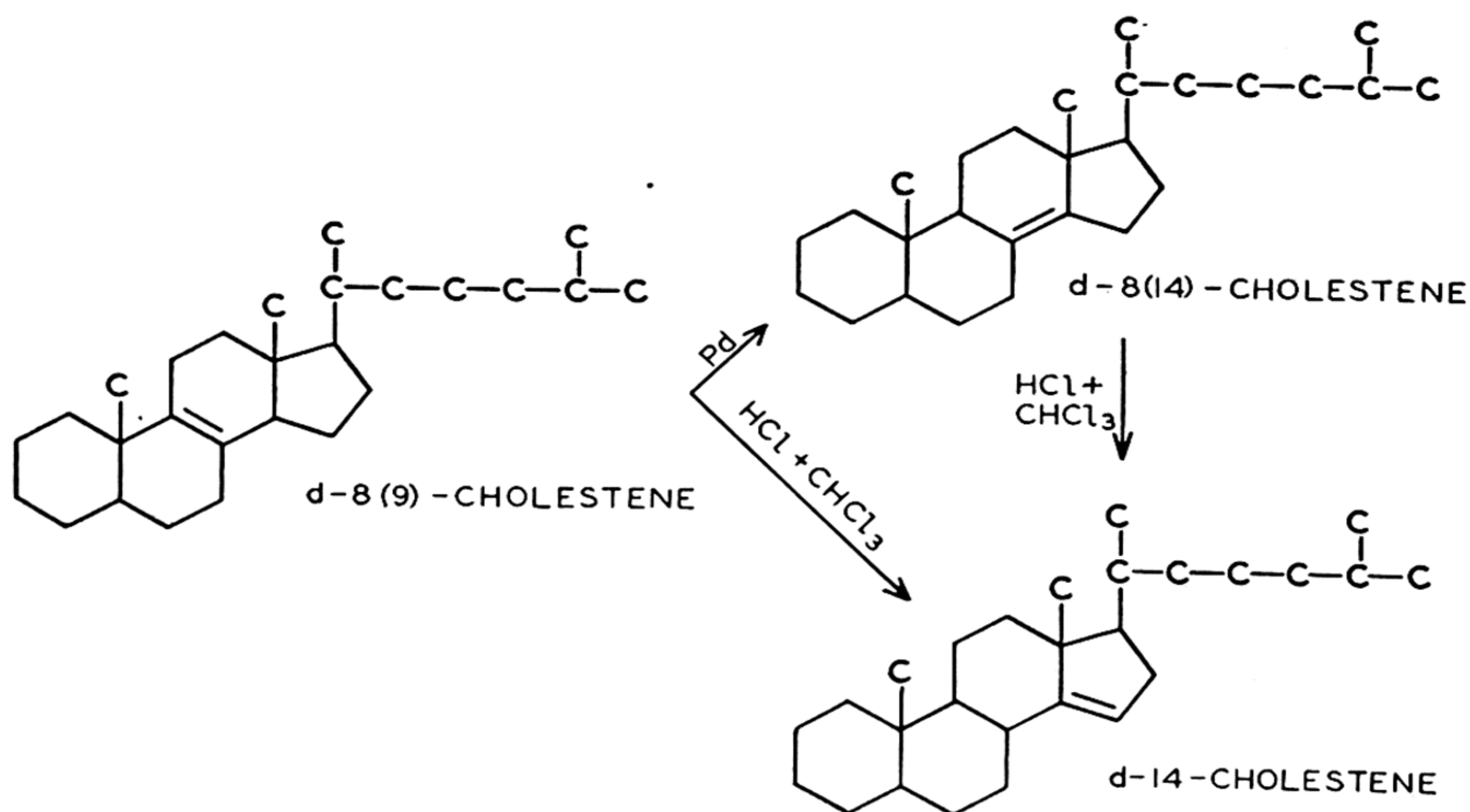
reported by C. S. Marvel and L. A. Brooks [*J. Am. Chem. Soc.*, **63**, 2630-2632 (1941)]. Treatment of a $C_{10}H_{16}$ (b.p. $172-175^{\circ}$, $n_D^{20} = 1.4655$) having the presumable structure of 1-(3-butenylidene)cyclopentane or 1-(3-butenyl)cyclopentene-1 gave an unsubstituted spiro[4.5]decene with unlocated double bond (there are 4 possibilities). Similarly, a $C_{11}H_{18}$ (b.p. $186-189^{\circ}$, $n_D^{20} = 1.4595$) presumably having the structure of 1-(3-butenylidene)-3-methylcyclopentane or 1-(3-butenyl)-3-methylcyclopentene-1 yielded a 2-methylspiro[4.5]decene with unlocated double bond (there are more than 4 possible structures).

Papers I and II of L. A. Goldblatt and S. Palkin on the vapor-phase thermal isomerization of α - and β -pinenes, originally presented before the Division of Organic Chemistry of the American Chemical Society, St. Louis Meeting, April 7-11, 1941, have been published in full [*J. Am. Chem. Soc.*, **63**, 3517-3522 (1941)]. The purified pinenes used in their investigation had the following properties:

d - α -pinene $[\alpha]_D = +32.06^{\circ}$, $D_4^{20} = 0.8600$, $n_D^{20} = 1.4645$;
 l - β -pinene $[\alpha]_D = -21.80^{\circ}$, $D_4^{20} = 0.8712$, $n_D^{20} = 1.4782$.

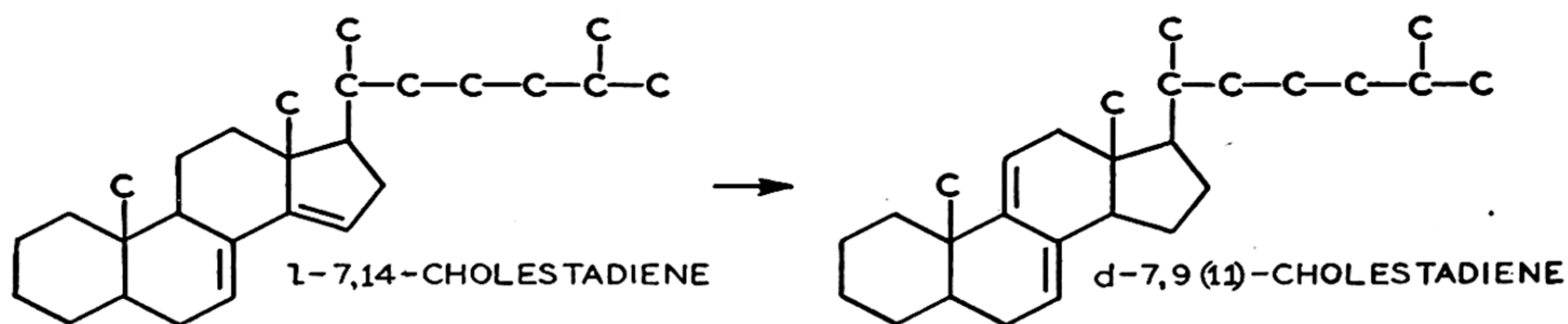
The d - α -pinene had a low specific rotation, indicating the presence of either some l - α -pinene or a terpene of very low rotatory power.

An article of Y. R. Naves and E. Perrottet [*Helv. Chim. Acta*, **24**, 789-804 (1941)] claims that caryophyllene from oil of cloves is just one chemical individual. It has two double bonds (not conjugated) distributed in the ring and as an "isopropylidene" group. The ring cannot have 7 carbon atoms, in the opinion of these investigators. They have succeeded in isomerizing tetrahydrocaryophyllene at room temperature in the presence of 50 per cent of its weight in aluminum chloride for 72 hours.

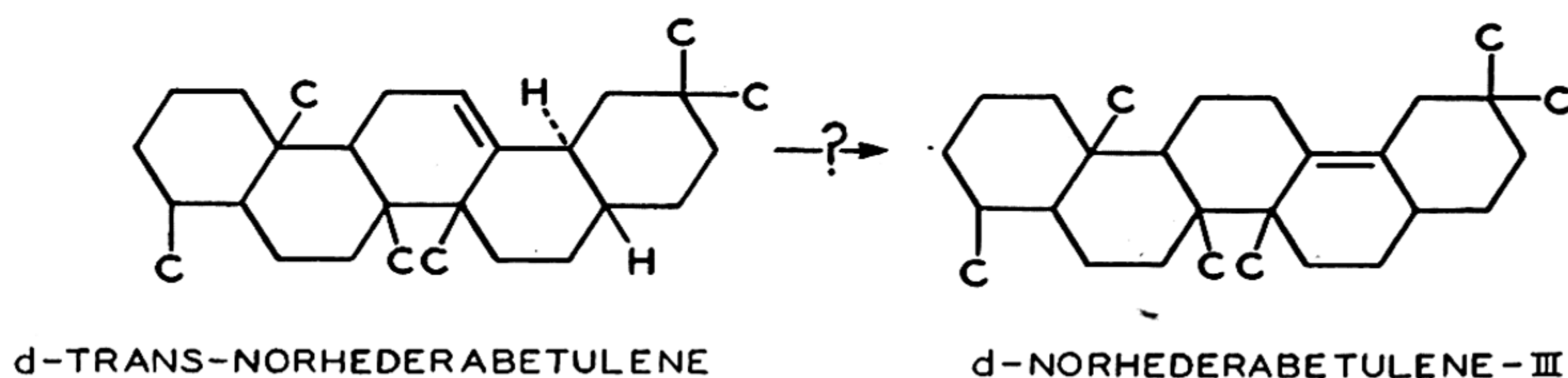


d-8(9)-Cholestene was isomerized to 90 per cent of *d*-8(14)-cholestene when subjected to a palladium catalyst in the presence of ethyl acetate and hydrogen, but formed 42 per cent of *d*-14-cholestene besides a cholestanol when dry hydrogen chloride was passed through its solution in chloroform at 0°, according to J. C. Eck and E. W. Hollingsworth [*J. Am. Chem. Soc.*, **63**, 2986-2990 (1941)]. *d*-14-Cholestene was produced to the extent of 30 per cent when a chloroform solution of *d*-8(14)-cholestene was treated with hydrogen chloride gas. (Structures on p. 429.)

l-7,14-Cholestadiene, $[\alpha]_D^{21} = -93.2^\circ$, yielded 48 per cent of an isomer with $[\alpha]_D^{24} = +27.3^\circ$, probably *d*-7,9(11)-cholestadiene, besides a maleic anhydride adduct, when heated under reflux with maleic anhydride in the presence of toluene for 10 hours in the work of J. C. Eck and E. W. Hollingsworth [*J. Am. Chem. Soc.*, **64**, 140-144 (1942)]. The instability of *l*-7,14-cholestadiene was also indicated by a lowered specific rotation, $[\alpha]_D = -69^\circ$, upon repeated recrystallization.

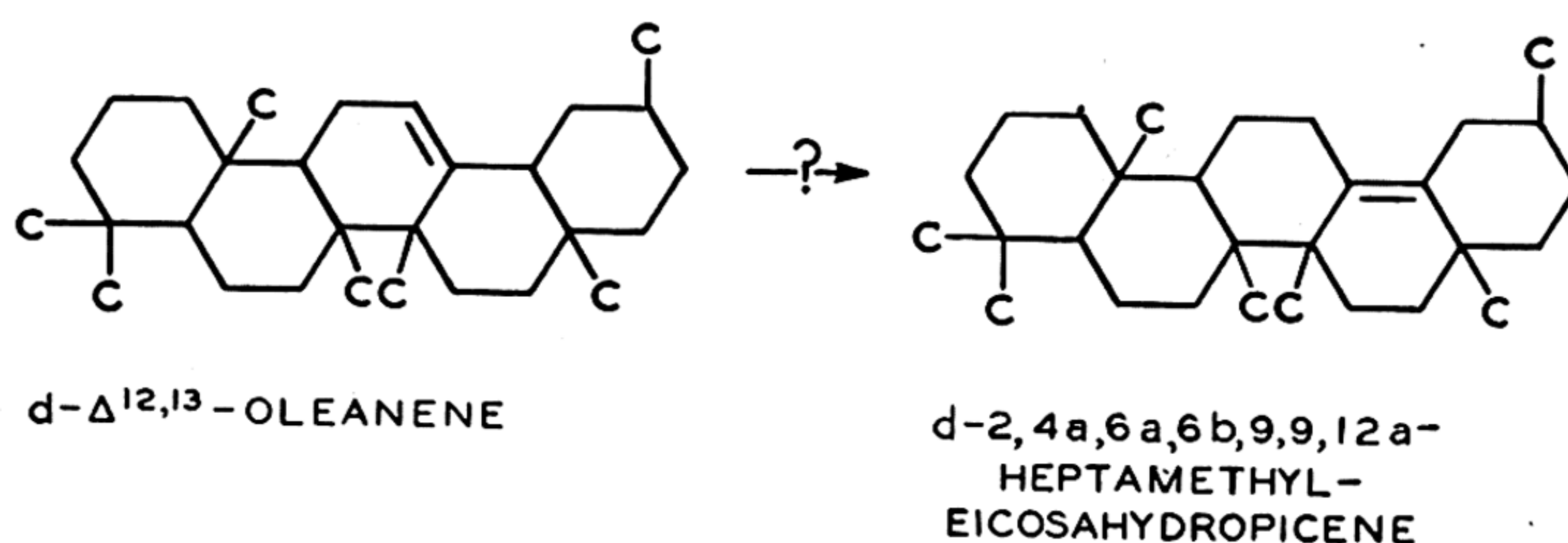


Further work on isomerizations of the pentacyclenes has been conducted by P. Bilham and G. A. R. Kon [*J. Chem. Soc.*, 1941, 552-561]. These investigators have found that *d*-*trans*-norhederabetulene, which is apparently a lower homolog of *d*- $\Delta^{12,13}$ -oleanene, is isomerized to "*d*-norhederabetulene-III" when boiled with acetic containing hydrochloric acid and amalgamated zinc:



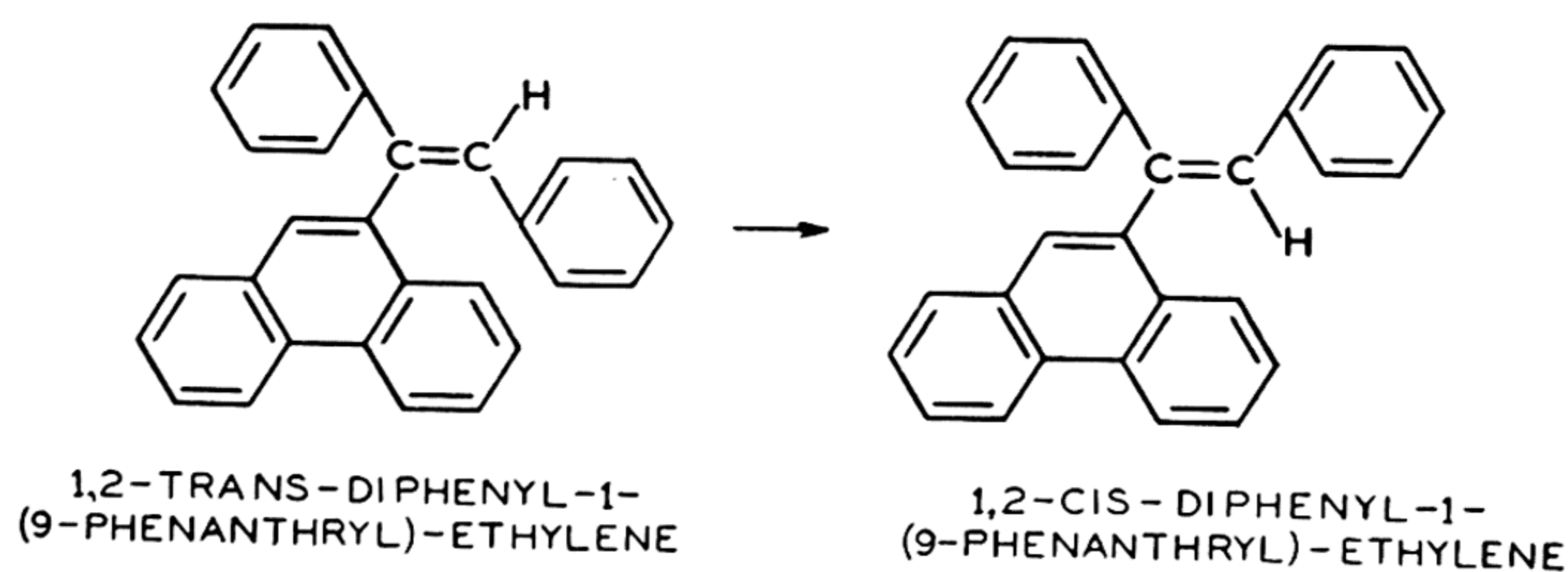
The proposed structures are based upon the probable identity of deoxy-quillaic and echinocystic acids, which calls for a *d*-4a,14b-*trans*-2,2,6a,6b,9,12a-hexamethyl-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-eicosahydricene structure for *d*-*trans*-norhederabetulene and a *d*-2,2,6a,6b,9,12a-hexamethyl-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14-eicosahydricene structure for "*d*-norhederabetulene-III." This formulation provides another explanation of the isomerizations and struc-

tures of the *cis* and *trans* forms of $\Delta^{12,13}$ -oleanene discussed in the Penta-cyclenes section of Chapter V, namely, the conversions of *d*-4a,14b-*cis*- and *d*-4a,14b-*trans*-2,4a,6a,6b,9,9,12a-heptamethyl-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-eicosahydronicenes into *d*-2,4a,6a,6b,9,9,12a-heptamethyl-1-2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14-eicosahydronicene:



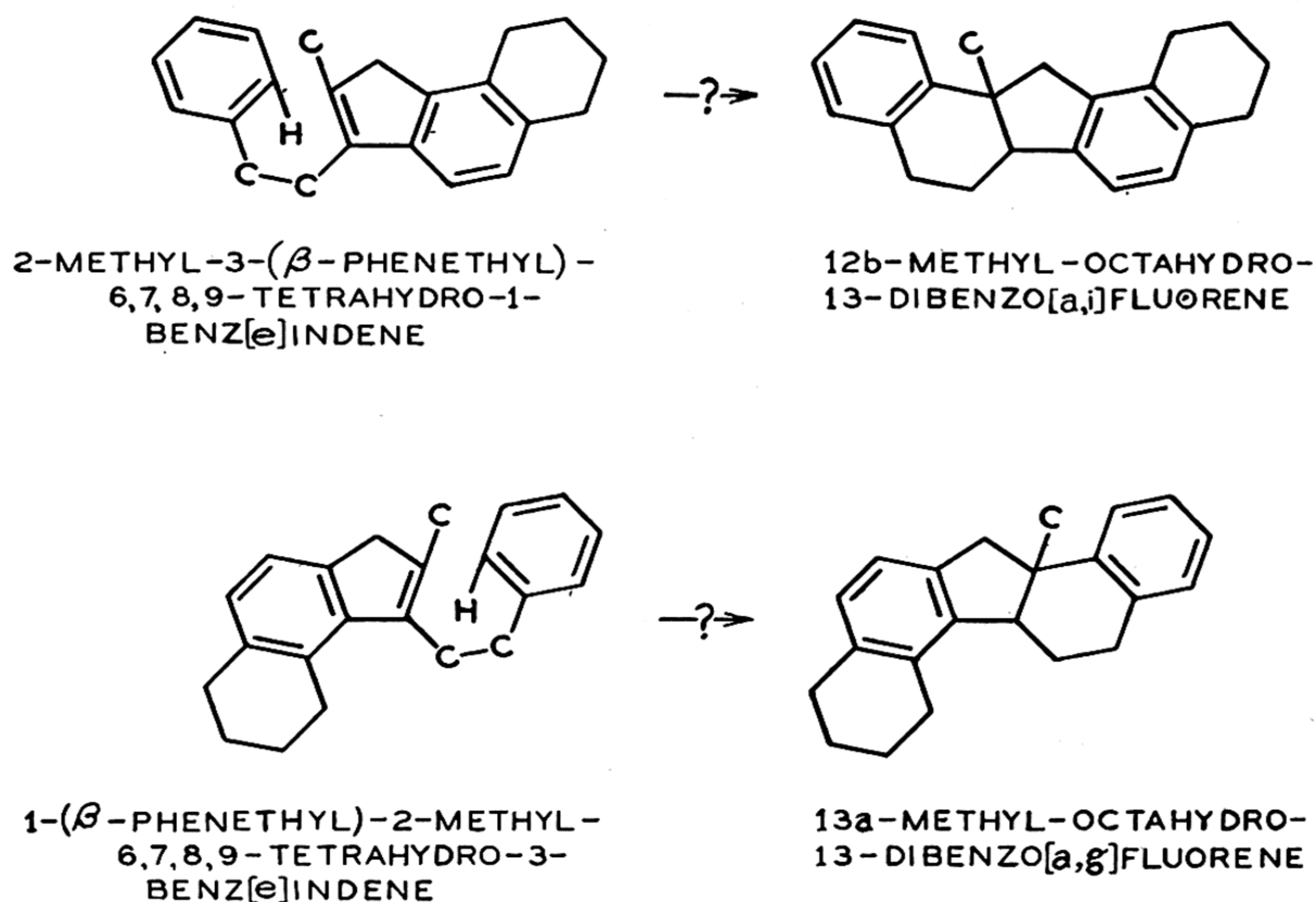
The action of aluminum chloride on polyalkylbenzenes at 70-75° has been studied by D. Nightingale and F. Wadsworth [*J. Am. Chem. Soc.*, 63, 3514-3517 (1941)]. They report that 1,2,3,5- and 1,2,4,5-tetramethylbenzenes, the 1,2,4- and 1,3,5-triethylbenzenes, and the 1,2,3,5- and 1,2,4,5-tetraethylbenzenes are pairs of hydrocarbons exhibiting partial reversibility in direction of isomerization. 1,2,3,4-Tetramethylbenzene and 1,2,3,4-tetraethylbenzene yielded the corresponding 1,2,3,5- and 1,2,4,5-tetraalkylbenzene isomers, with little if any of the original 1,2,3,4-hydrocarbon. These results are of interest in the interpretation of Friedel-Crafts alkylations of polyalkylbenzenes.

1,2-*Trans*-diphenyl-1-(9-phenanthryl)-ethylene (*i.e.*, 1-phenyl-(*cis*-1-[9-phenanthryl]-2-phenyl)-ethylene, m.p. 140°) underwent an isomerization to 1,2-*cis*-diphenyl-1-(9-phenanthryl)-ethylene (*i.e.*, 1-phenyl-(*trans*-1-[9-phenanthryl]-2-phenyl)-ethylene, m.p. 166 - 167°) when heated under reflux for two hours with nitrobenzene containing iodine, according to F. Bergmann [*J. Am. Chem. Soc.*, 64, 69-72 (1942)]. The greater repulsion of the *cis* phenyl and phenanthryl groups as compared with two *cis* phenyl groups is an interesting phenomenon:



A cyclization of 2-methyl-3-(β -phenethyl)-6,7,8,9-tetrahydro-1-benz[e]indene and/or 1-(β -phenethyl)-2-methyl-6,7,8,9-tetrahydro-3-benz-

[e]indene at 0° in the presence of aluminum chloride and carbon disulfide is indicated in the work of R. H. Martin [*J. Chem. Soc.*, 1941, 679-685]. The structure of the product is unestablished; it may be that of 12b-methyl-1,2,3,4,6b,7,8,12b-octahydro-13-dibenzo[a,i]fluorene and/or 13a-methyl-5,6,6a,7,8,9,10,13a-octahydro-13-dibenzo[a,g]fluorene, respectively. A selenium dehydrogenation of the product at 305° for 20 hours yielded only a small amount of an aromatic hydrocarbon (m.p. 306-308°), obviously neither the expected 13-dibenzo[a,i]fluorene (m.p. 234°) nor the expected 13-dibenzo[a,g]fluorene (m.p. 172°).

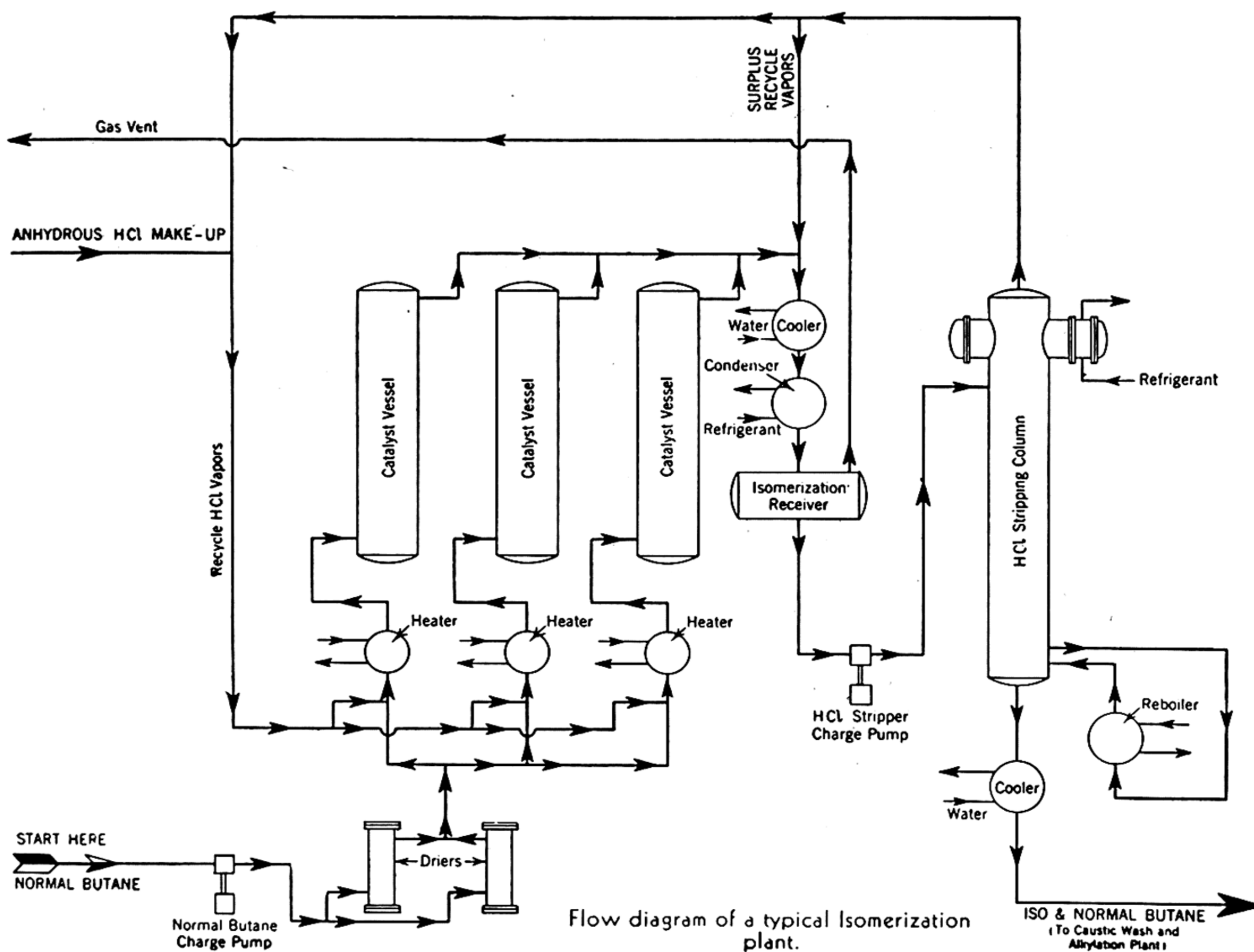


APPLIED ISOMERIZATION

The National Defense program of the United States calls for the isomerization of all available *n*-butane and *n*-pentane to obtain isobutane and isopentane for aviation gasoline. There are several commercial isomerization plants that produce these products at the present time. They utilize the Shell Oil Co., Inc., and the Universal Oil Products Co. processes. The Standard Oil Co. (Indiana) is also a process licensor [*Anon.*, *Natl. Petroleum News*, 33, No. 51, pp. 9 and 20 (1941)].

A number of isomerization units are being utilized for the production of isobutane from *n*-butane. A flow chart of a typical isomerization plant for converting *n*-butane into isobutane is included. Vapors of *n*-butane are passed over a granular mass containing aluminum chloride on an inorganic support. Hydrogen chloride gas is continuously recycled to the reaction zone. In single-pass operation, under the reaction conditions usually prevailing in the catalyst chambers, about 40-45 per cent of the *n*-butane input is isomerized to isobutane. With intermediary frac-

tionation, 90 per cent of the *n*-butane can be isomerized to isobutane. [L. J. Coulthurst, *Natl. Petroleum News*, 33, No. 52, R-403, R-404, and R-406 (1941); *Petroleum Eng.*, 13, No. 4, 113, 116, 118 (1942); Bulletin 0-41-13 Foster Wheeler Corp., New York. J. C. Morrell and G. Egloff, *World Petroleum*, 12, No. 11, 70-75 (1941).]



Flow diagram of a typical Isomerization plant.

The Standard Oil Co. (Indiana) has reported that their process increases the octane number of straight-run gasoline from 65 to around 81, with 98 per cent yield in the isomerization. An aviation gasoline formerly containing 35 per cent of base stock and 65 per cent of synthetic hydrocarbons (isopentane, 2,2,4-trimethylpentane, or "alkylate") can now be produced with 60 per cent of base stock (isomerized). The 25 per cent of the enumerated synthetic hydrocarbons so conserved are available for the further production of an additional 62.5 per cent of aviation gasoline. [N.P.N. News Bureau, *Natl. Petroleum News*, 33, No. 50, 18 (1941). Anon., *Oil Gas J.*, 40, No. 31, 41 (1941); 40, No. 36, 30 (1942).]

The Applied Isomerization supplement concludes with a series of interesting, representative digests of patents. Each of the patented processes involves an isomerization of hydrocarbons or of their closest deriva-

tives; but this may be preceded, masked, or supplemented by other chemical reactions. A list of United States and foreign patents on isomerization of hydrocarbons and indices of the specified charging stocks and catalysts is given, corresponding to the concluding patent digests.

PATENT NUMBER INDEX

<i>Australian</i>	<i>Canadian</i>	<i>Russian</i>
106,671	384,317	51,181
113,275	399,051	<i>Swiss</i>
<i>Austrian</i>	<i>Dutch</i>	153,193
72,293	48,338	<i>United States</i>
131,128	48,509	
<i>British</i>	48,706	1,985,792
18,356 (1911)	50,385	2,105,850
18,653 (1912)	Application 83,778	2,164,334
347,108	Application 83,820	2,175,359
356,020	Application 86,418	2,186,022
367,593	Application 87,959	2,199,132
501,896	<i>French</i>	2,216,131
510,478	17,233	2,216,285
516,659	450,431	2,216,470
516,780	713,357	2,220,090
517,758	837,202	2,220,091
525,554	840,717	2,220,092
526,215	852,114	2,238,860
527,767	854,936	2,249,366
527,954	<i>German</i>	2,250,118
528,178	263,017	2,250,410
529,914	548,901	2,257,896
530,253	596,820	2,260,279
534,151	Application J. 61,782	2,263,026
535,054	<i>Hungarian</i>	2,265,548
535,394	Application P. 9,689	2,265,870
535,398	<i>Italian</i>	2,266,011
Application 12092/40	365,253	2,266,012
		2,268,401
		2,271,043

INDEX OF HYDROCARBONS OR DERIVATIVES ISOMERIZED IN THE
PATENTED PROCESSES

<i>Alkanes</i>	U. S. 2,199,132	British 535,394
<i>n</i> -Butane	U. S. 2,216,470	Dutch 48,338
British 516,659	U. S. 2,238,860	Dutch 48,706
British 516,780	U. S. 2,249,366	Dutch 50,385
British 525,554	U. S. 2,250,118	U. S. 2,250,118
British 527,767	U. S. 2,257,896	U. S. 2,250,410
British 528,178	U. S. 2,265,548	U. S. 2,265,870
British 535,054	U. S. 2,266,011	U. S. 2,271,043
British 535,394	U. S. 2,266,012	
British Application 12092/40	U. S. 2,268,401	<i>n</i> -Hexane
Canadian 399,051	U. S. 2,271,043	British 527,767
Dutch 48,338	Isobutane	British 535,054
Dutch 50,385	British 527,767	U. S. 2,250,410
Dutch Application 83,820	<i>n</i> -Pentane	U. S. 2,268,401
Dutch Application 86,418	British 526,215	<i>n</i> -Heptane
French 840,717	British 527,954	U. S. 2,268,401
Italian 365,253	British 528,178	<i>n</i> -Octane
	British 535,054	British 535,054

"C ₄ -C ₆ " Australian 113,275 Hungarian Application P. 9,689	Naphtha or straight-run gasoline British 535,054 British 535,394 U. S. 2,260,279 U. S. 2,266,012 U. S. 2,268,401 U. S. 2,271,043	<i>Alkadienes</i> 3-Methylbutadiene-1,2 British 18,356
"C ₄ -C ₉ " U. S. 2,250,118		<i>Alkynes</i> 3-Methylbutyne French 17,233
"C ₄ -C ₁₂ " British 527,767		<i>Cyclanes</i> British 529,914
"Boiling below 100° C" Dutch 48,338	<i>Alkenes</i>	<i>Terpenes and Hydroterpenes</i>
"Boiling below 160° C" British 527,954 Dutch 48,706 French 854,936 U. S. 2,250,410	Butenes British 501,896 Canadian 384,317 Dutch Application 83,778 Russian 51,181 U. S. 2,216,285	Menthene-1 Austrian 131,128 British 367,593 French 713,357 German 548,901 Swiss 153,193
"Boiling below 200° C" British 526,215 British 535,054 Hungarian Application P. 9,689	Pentenenes Austrian 72,293 British 18,653 German 263,017	α -Pinene U. S. 1,985,792
Unspecified alkanes British 530,253 British 535,394 British 535,398 British Application 12092/40 Canadian 399,051 French 852,114 U. S. 2,268,401	Hexenes British 18,653	β -Pinene U. S. 1,985,792
Alkane mixture with naphthenes and/or aromatics U. S. 2,260,279	Octene British 501,896	Terpenes German 596,820
	Unspecified alkenes Australian 106,671 British 501,896 British 510,478 Dutch Application 83,778 French 837,202 Russian 51,181 U. S. 2,263,026	<i>Miscellaneous</i> Chlorinated naphtha U. S. 2,164,334 "Polynuclear and cyclic compounds" of the hydroaromatic series U. S. 2,216,131 Rubber British 347,108

INDEX OF CATALYTIC MATERIALS USED IN THE PATENTED ISOMERIZATIONS

Acid phosphates of metals of periodic group 1 to 3 Russian 51,181	Alumina, silica, and thoria U. S. 2,216,285
Acid sulfates of metals of periodic groups 1 to 3 Russian 51,181	Alumina with cobalt U. S. 2,175,359
Activated carbon carriers for catalysts British 527,767 German Application J. 61,782	Alumina with molybdena U. S. 2,175,359
Alkali halide with aluminum halide British 526,215 British 530,253 Dutch 48,338 Dutch 50,385	Aluminum bromide (<i>See also</i> Aluminum halides) Dutch Application 83,820
	Aluminum bromide with hydrogen U. S. 2,271,043
Hungarian Application P. 9,689 U. S. 2,266,011 U. S. 2,266,012 U. S. 2,268,401	Aluminum chloride (<i>See also</i> Aluminum halides) British 527,954 Dutch Application 83,820 French 854,936
Alkali halides with Friedel-Crafts catalysts U. S. 2,268,401	U. S. 2,216,470 U. S. 2,250,410 U. S. 2,271,043
Alumina British 18,356 British 18,653 British Application 12092/40 Canadian 399,015	Aluminum chloride dissolved in liquid hydrogen halide U. S. 2,257,896
German 263,017 U. S. 2,105,850 U. S. 2,263,026 U. S. 2,271,043	Aluminum chloride on carriers British 516,659 British 517,758 Canadian 399,051
Alumina activated by acid British 534,151	Dutch Application 86,418 U. S. 2,271,043
	Aluminum chloride with ferric chloride British 528,178

- Aluminum chloride with hydrogen
U. S. 2,271,043
- Aluminum chloride with hydrogen chloride or hydrogen halide
U. S. 2,271,043
- Aluminum chloride with hydrogen chloride and hydrogen
U. S. 2,271,043
- Aluminum chloride with kaolin, hydrogen chloride, and hydrogen
U. S. 2,271,043
- Aluminum halides (*See also* Aluminum bromide, Aluminum chloride)
Australian 113,275 Dutch 50,385
British 516,780 French 840,717
British 525,554 Italian 365,253
British 529,914 U. S. 2,199,132
British 530,253 U. S. 2,249,366
British 534,151 U. S. 2,250,410
British 535,054 U. S. 2,257,896
British 535,398 U. S. 2,260,279
Dutch 48,706 U. S. 2,271,043
- Aluminum halide and hydrocarbon complex
British 525,554 French 852,114
British 526,215 U. S. 2,250,118
British 529,914 U. S. 2,260,279
British 530,253 U. S. 2,271,043
Dutch 48,338
- Aluminum halide oxonium compounds
British 347,108
- Aluminum halide with aluminum, beryllium, copper, iron, magnesium, or zinc
U. S. 2,271,043
- Aluminum halide with "Ansolvo acids"
U. S. 2,271,043
- Aluminum halide with hydrogen
Australian 113,275 Hungarian Application P. 9,689
British 529,914 U. S. 2,260,279
British 535,054 U. S. 2,271,043
British 535,398
Dutch 50,385
- Aluminum halide with hydrogen halide
See Hydrogen halide with aluminum halides
- Aluminum metal with aluminum halide
U. S. 2,271,043
- Aluminum metal with hydrogen chloride
U. S. 2,271,043
- Aluminum metal with hydrogen chloride and hydrogen
U. S. 2,271,043
- Aluminum metal with hydrogen halide
Hungarian Application P. 9,689
- Aluminum salts of boric, phosphoric, or sulfuric acids
U. S. 2,216,470
- Aluminum silicate (*See also* Clay, Permutite, Zeolites)
Australian 106,671 Dutch Application 83,778
British 501,896 U. S. 2,216,470
British 534,151
Canadian 399,051
- Aluminum silicate with chromia, molybdena, tungsten oxide, or periodic group 6 sulfides
British 534,151
- Aluminum silicate with Friedel-Crafts catalysts
British 534,151
- Ammonium thiomolybdate with active carbon
British 527,767
- Ammonium tungstate
German 596,820
- Antimony halide
U. S. 2,250,410
U. S. 2,257,896
U. S. 2,271,043
- Arsenic halide
U. S. 2,250,410
U. S. 2,257,896
- Bauxite
British Application 12092/40
German Application J. 61,782
U. S. 2,271,043
- Beryllium chloride
British 527,954
French 854,936
U. S. 2,257,896
- Beryllium halide
U. S. 2,250,410
U. S. 2,271,043
- Beryllium with an aluminum halide
U. S. 2,271,043
- Bismuth halide
U. S. 2,257,896
- Boron halides
U. S. 2,250,410
U. S. 2,257,896
U. S. 2,271,043
- Cadmium halide
U. S. 2,250,410
U. S. 2,257,896
- Cerium halide
U. S. 2,257,896
- Chromia with aluminum silicate
British 534,151
- Chromia with metal sulfide
German Application J. 61,782
- Chromium halide
Italian 365,253
U. S. 2,216,470
U. S. 2,257,896
- Chromium salts of boric or silicic acids
U. S. 2,216,470
- Chromium salts of phosphoric or sulfuric acids
Russian 51,181
U. S. 2,216,470
- Clay (*See also* Fuller's earth and Kaolin)
British 516,659
Canadian 399,051
German Application J. 61,782
U. S. 2,271,043
- Cobalt halide
U. S. 2,257,896

- Cobalt phosphate or sulfate
 Russian 51,181
 Cobalt with alumina
 U. S. 2,175,359
 Copper
 French 713,357
 German 548,901
 Copper halide
 U. S. 2,216,470
 U. S. 2,257,896
 Copper phosphate
 French 713,357
 German 548,901
 U. S. 2,216,470
 Copper salts of boric, silicic, or sulfuric acids
 U. S. 2,216,470
 Copper with an aluminum halide
 U. S. 2,271,043
 Dehydrogenating catalysts
 British 527,767
 Fuller's earth
 British 356,020
 British Application 12092/40
 U. S. 2,271,043
 Gallium halide
 U. S. 2,257,896
 Germanium halide
 U. S. 2,257,896
- Halides
- See*
 Alkali halide
 Alkyl halide
 Aluminum bromide
 Aluminum chloride
 Aluminum halides
 Antimony halide
 Arsenic halide
 Beryllium chloride
 Beryllium halide
 Bismuth halide
 Boron halides
 Cadmium halide
 Cerium halide
 Chromium halide
 Cobalt halide
 Copper halide
 Gallium halide
 Germanium halide
 Hydrogen halide
 Indium halide
 Iron halides
 Lead halide
 Hydrogenating catalysts
 British 527,767
 U. S. 2,175,359
 Hydrogen halide, solution of metal halide in liquid
 U. S. 2,257,896
 Manganese salts of boric, hydrochloric, or silicic acids
 Mercury halide
 Metal halides
 Molybdenum halide
 Nickel halide
 Niobium halide
 Phosphorus halide
 Selenium halide
 Silicon halide
 Silver halide
 Sulfur halide
 Tantalum halide
 Tellurium halide
 Tin chloride
 Tin halide
 Titanium halide
 Tungsten halide
 Uranium halide
 Vanadium halide
 Zinc halides
 Zirconium halide
- Hydrogen halide with acid-acting halides
 U. S. 2,250,410
 Hydrogen halide with aluminum halides
 British 516,659
 British 525,554
 British 526,215
 British 527,954
 British 528,178
 British 529,914
 British 530,253
 British Application 12092/40
 Dutch 48,338
 Dutch 48,706
 French 854,936
 Hungarian Application P. 9,689
 U. S. 2,199,132
 U. S. 2,249,366
 U. S. 2,250,118
 U. S. 2,257,896
 U. S. 2,260,279
 U. S. 2,266,011
 U. S. 2,266,012
 U. S. 2,271,043
 Hydrogen halide with aluminum halide and a metal
 U. S. 2,265,548
 U. S. 2,265,870
 Hydrogen with alumina or phosphoric acid
 U. S. 2,263,026
 Hydrogen with aluminum bromide or with aluminum chloride
 U. S. 2,271,043
 Hydrogen with aluminum halides
 Australian 113,275
 British 529,914
 British 535,054
 British 535,398
 Dutch 50,385
 Hungarian Application P. 9,689
 U. S. 2,260,279
 U. S. 2,271,043
 Hydrogen with tungsten disulfide
 British 527,767
 Indium halide
 U. S. 2,257,896
 Iron halides
 British 527,954
 British 528,178
 French 854,936
 Italian 365,253
 U. S. 2,105,850
 U. S. 2,216,470
 U. S. 2,250,410
 U. S. 2,257,896
 Iron phosphate or sulfate
 Russian 51,181
 U. S. 2,216,470
 Iron salts of boric or silicic acids
 U. S. 2,216,470
 Iron with an aluminum halide
 U. S. 2,271,043
 Kaolin
 British Application 12092/40
 U. S. 2,271,043
 Lead halide
 U. S. 2,257,896
 Magnesia
 German Application J. 61,782
 Magnesite
 German Application J. 61,782
 Magnesium with an aluminum halide
 U. S. 2,271,043
 Manganese phosphates or sulfates
 Russian 51,181
 U. S. 2,216,470
 Manganese salts of boric, hydrochloric, or silicic acids
 U. S. 2,216,470

- Mercury halide
U. S. 2,257,896
- Metal halide (solution in liquid hydrogen halide)
U. S. 2,257,896
- Metal halides (For specific metal halides see those listed under "Halides")
British 535,394
- Molybdena with alumina
U. S. 2,175,359
- Molybdenum halide
British 527,954 U. S. 2,250,410
French 854,936 U. S. 2,257,896
U. S. 2,216,470
- Molybdenum salts of boric, phosphoric, silicic, or sulfuric acids
U. S. 2,216,470
- Molybdenum sulfur compounds
See Ammonium thiomolybdate
- Nickel halide
U. S. 2,216,470
U. S. 2,257,896
- Nickel phosphate or sulfate
Russian 51,181
U. S. 2,216,470
- Nickel salts of boric or silicic acids
U. S. 2,216,470
- Niobium halide
U. S. 2,271,043
- Oxonium compounds of organic substances with aluminum halides, stannic chloride, or sulfuric acid
British 347,108
- Permutite
Australian 106,671
British 501,896
Dutch Application 83,778
U. S. 2,271,043
- Phosphates
See
Acid phosphates
Aluminum salts of boric, phosphoric, or sulfuric acids
Chromium salts of phosphoric or sulfuric acids
Cobalt phosphate or sulfate
Copper phosphate
Iron phosphate or sulfate
Manganese phosphates or sulfates
Molybdenum salts of boric, phosphoric, silicic, or sulfuric acids
Nickel phosphate or silicate
Zinc salts of boric, phosphoric, silicic, or sulfuric acids
- Phosphoric acid
Russian 51,181
U. S. 2,263,026
- Phosphoric acid on carrier
British 534,151 Russian 51,181
Canadian 384,317 U. S. 2,186,022
- Phosphorus halide
U. S. 2,257,896
- Phosphotungstic acid
U. S. 1,985,792
- Pumice
British 517,758
British Application 12092/40
French 713,357
German 548,901
German Application J. 61,782
- Selenium halide
U. S. 2,257,896
- Silica (See also "Alumina, silica, and thoria" and Silica gel)
British Application 12092/40
- Silica gel
British 534,151
German Application J. 61,782
U. S. 2,271,043
- Silicon halide
U. S. 2,257,896
- Silver halide
U. S. 2,257,896
- Sulfates
See
Acid sulfates
Aluminum salts of boric, phosphoric, or sulfuric acids
Chromium salts of phosphoric or sulfuric acids
Cobalt phosphate or sulfate
Copper salts of boric, silicic, or sulfuric acids
Iron phosphate or sulfate
Manganese phosphates or sulfates
Molybdenum salts of boric, phosphoric, silicic, or sulfuric acids
Nickel phosphate or sulfate
Zinc salts of boric, phosphoric, silicic, or sulfuric acids
Sulfides of metals of periodic groups 2 to 8
German Application J. 61,782
Sulfides of metals of periodic groups 6 to 8
British 527,767
British 534,151
- Sulfur halide
U. S. 2,257,896
- Sulfuric acid
British 510,478
French 837,202
- Sulfuric acid oxonium compounds
British 347,108
- Tantalum halide
U. S. 2,257,896
U. S. 2,271,043
- Tellurium halide
U. S. 2,257,896
- Thoria
See "Alumina, silica, and thoria"
- Tin chloride
French 854,936
- Tin chloride oxonium compounds
British 347,108

Tin halides		Water with aluminum halide
British 527,954		British 516,659
U. S. 2,257,896		British 517,758
Titanium halide		Zeolites (<i>See also</i> Permutite)
U. S. 2,257,896		Australian 106,671
Tungsten disulfide		British 356,020
British 527,767		British 501,896
Tungsten halide		Dutch Application 83,778
British 527,954	U. S. 2,250,410	Zinc halides
French 854,936	U. S. 2,257,896	British 527,954
		U. S. 2,250,410
		French 854,936
		U. S. 2,257,896
		U. S. 2,216,470
		U. S. 2,271,043
Tungsten oxide or sulfide		Zinc salts of boric, phosphoric, silicic, or
British 534,151		sulfuric acids
Tungstic acid		U. S. 2,216,470
U. S. 1,985,792		Zinc with an aluminum halide
Uranium halide		U. S. 2,271,043
U. S. 2,257,896		Zirconium halide
Vanadium halide		U. S. 2,257,896
U. S. 2,257,896		U. S. 2,271,043

DIGESTS OF PATENTS

Australian Patents

N. V. de Bataafsche Petroleum Maatschappij, (assignee of H. Hoog), Australian Patent 106,671:

Isomerization.

Production of branched or more highly branched alkenes or alkene-containing mixtures with hydrated aluminum silicates of the permutite or zeolite type, particularly hydrated alkali aluminum silicates, at 275-500° C.

N. V. de Bataafsche Petroleum Maatschappij, (assignee of A. J. van Peski and C. A. Schuit), Australian Patent 113,275:

Isomerization.

Preventing the formation of undesirable by-products when producing saturated hydrocarbons with branched or more highly branched chains from saturated hydrocarbons boiling below 200° C. and preferably containing 4 to 6 carbon atoms by reacting at not above 200° C. in the presence of hydrogen, using aluminum halides as catalysts.

Austrian Patents

Badische Anilin- und Soda-Fabrik, Austrian Patent 72,293 of Aug. 25, 1916, British Patent 18,653 of Aug. 14, 1912, French Patent 450,431 of Jan. 19, 1912, German Patent 263,017 of July 28, 1913, and U. S. Patent 1,102,655 of July 7, 1914:

Production of isopentenes and their derivatives.

n-Pentenes are converted into isomeric alkenes, especially 2-methylbutene-2, by heating to elevated temperatures, in the presence of catalysts. Instead of *n*-pentenes, substances yielding it may be used.

n-Pentenes are produced from monochloro-*n*-pentane by passage over lime at elevated temperature. These pentenes give 2-methylbutene-2 when passed over calcined alumina at 450° C.; the hexenes from monochloro-*n*-hexane yielded a distillate which upon treatment with concentrated aqueous hydrogen chloride gave 3-chloro-3-methylpentane. 2-Methylbutene-2 is produced by passing over heated alumina the alcohol derived from methyl-*n*-propyl ketone. [*Chem. Zentr.*, 1913, II, 729; *Chem. Abs.*, 8, 1331 (1914); 8, 553 (1914); 11, 870 (1917); Friedlaender's *Fortschritte der Teerfarbenfabrikation*, 11, 810-811 (1915).]

Schering-Kahlbaum A.-G., Austrian Patent 131,128 of March 11, 1931 (July 15, 1923), British Patent 367,593 of Feb. 25, 1932, French Patent 713,357 of March 16, 1931, German Patent 548,901 of March 21, 1930, Swiss Patent 153,193 of March 9, 1931:

Process for the preparation of menthene-3.

Menthene-1 is heated to a high temperature (above 300° C.) in the presence of a catalyst such as pumice stone, copper, or a copper phosphate. Menthene-3 is separated by fractionation from the mixture of isomeric menthenes formed [*Chem. Abs.*, 26, 1626, 4069 (1932); *Chem. Zentr.*, 1932, I, 3916; Friedlaender's *Fortschritte der Teerfarbenfabrikation*, 18, 581-582 (1933).]

British Patents

Badische Anilin- und Soda-Fabrik, British Patent 18,356, Aug. 14, 1911: 2-Methylbutene-2, the 3-methylbutadiene-1,2, the 2-methylbutadiene-1,3, and halogenisopentanes.

Isoprene is produced by monohalogenating isopentane, removing hydrogen halide, converting the resulting 2-methylbutene-2 into a dihalogenisopentane, then removing 2 mols of hydrogen halide by means of a catalytic agent such as barium chloride or alumina. If a mixture of isoprene and 3-methylbutadiene-1,2 results, the latter is converted into isoprene by the catalytic action of alumina or a compound containing it. [*Chem. Abs.*, 7, 425 (1913).]

I. G. Farbenindustrie A.-G., British Patent 347,108, Jan. 16, 1930:
Rubber isomerization.

Products which when vulcanized have good wearing qualities are obtained from rubber which is treated in suspension or solution at temperatures below 100° C. with organic-inorganic oxonium compounds, free from aldehyde groups and phenolic hydroxyl groups, preferably with exclusion of oxygen and suitably in the presence of inert organic solvents such as benzene. The oxonium compounds used may be obtained from aluminum halides, stannic chloride, concen-

trated sulfuric acid and the halides of carboxylic acids such as acetic anhydride, acetyl or phthalyl chlorides or phosgene or organic oxygen compounds such as ethers. [*Chem. Abs.*, 27, 448 (1933).]

Schering-Kahlbaum A.-G., British Patent 356,020, Oct. 24, 1930:

α -Pinene.

Nopinene or an oil containing it is heated in the presence of a catalyst comprising an inert porous carrier such as porous pottery, artificial zeolitic material or fuller's earth. [*Chem. Abs.*, 26, 5579 (1932).]

N. V. de Bataafsche Petroleum Maatschappij, British Patent 501,896, March 7, 1939:

Isomerization of alkenes.

Branched or more highly branched alkenes are obtained from non- or less-branched alkenes, *i.e.*, the products have more branch chains, by contacting alkenes with hydrated alkali aluminum silicates of the permutite or zeolite type at about 275-500° C. Gaseous or liquid alkenes, *e.g.*, butene, octene or alkene-containing mixtures such as a C₄ fraction of cracking gas or residual gas after polymerization thereof, and cracking gasoline may be treated. Products of gasoline boiling range can be used as such or as addition agents therefor, if desired, after hydrogenation. Isobutene obtained from *n*-butenes may be polymerized and hydrogenated to isoöctane. In examples, (1) a 50-50 mixture of *n*-butenes and butane is passed over granulated commercial sodium permutite at 450° with a contact time of 183 seconds, and (2) octene is similarly treated at 300° with a contact time of 1 minute. [*Chem. Abs.*, 33, 6338 (1939).]

Standard Oil Development Co., British Patent 510,478, Aug. 2, 1939:

Motor fuels.

Polymers of the nature of motor fuels are produced from hydrocarbon mixtures the alkene component of which consists of iso and normal alkenes of 3-5 carbon atoms by subjecting the mixture to the action of sulfuric acid at elevated temperature and pressure in such a manner as to ensure substantially complete polymerization of the isoalkenes and only partial or no polymerization of the *n*-alkenes, distilling off the polymers so formed and subjecting the residue, which contains substantially no isoalkenes to the action of sulfuric acid of 60-80 per cent concentration while at 76.7-162.8° C. and under pressure sufficient to maintain the alkene in liquid condition, whereby a substantial portion of the *n*-alkenes is isomerized and polymerized, and separating the polymer so produced. [*Chem. Abs.*, 34, 5274 (1940).]

N. V. de Bataafsche Petroleum Maatschappij, British Patent 516,659, Jan. 8, 1940:

A process for the manufacture of isobutane from *n*-butane.

Manufacture of isobutane from *n*-butane by contacting *n*-butane, preferably in the gaseous phase at temperatures below 200° C., with a catalyst. The catalyst consists of aluminum chloride mixed with or brought on to a carrier substance comprising an inorganic substance containing water which normally can only be split off at temperatures above 200° C., for example pipe clay dried at 300° C. Reaction may be carried out in the presence of small quantities of hydrogen chloride or water and elevated pressure may be used.

Texaco Development Corp., British Patent 516,780, July 7, 1938:

Preparation of alkylated hydrocarbons from *n*-alkanes.

Antiknock motor fuels are obtained by partly converting *n*-butane into isobutane in presence of a halide of aluminum, interaction of the isomerized portion with a C₄ alkene in presence of sulfuric acid or phosphoric acid, and recycling unchanged materials. [*Brit. Chem. Abs.-B*, 1940, 265).]

N. V. de Bataafsche Petroleum Maatschappij, British Patent 517,758, Feb. 7, 1940:

A process for the manufacture of isobutane from *n*-butane.

A vapor phase process characterized by passage of the *n*-butane over a solid catalyst containing aluminum chloride on a carrier, such as pumice, at temperatures below 200° C. and contact times of 20 seconds. Hydrogen chloride or water is added.

Texaco Development Corp., British Patent 525,554, Aug. 30, 1940:

Treatment of hydrocarbons.

Alkylation of isobutane with alkenes occurs in the presence of suitable catalysts in the presence of excess isobutane. Reaction products are separated and unreacted hydrocarbons are separated into *n*- and isobutane, the latter of which is recycled to the alkylation; the former is isomerized, suitably in the presence of 5-30 per cent, preferably 10 per cent of catalyst (aluminum bromide, aluminum chloride or their hydrocarbon compounds) either alone or in the presence of hydrogen chloride. Temperatures up to 93.3° C. may be used for the isomerization, but room temperature is preferred.

N. V. de Bataafsche Petroleum Maatschappij, British Patent 526,215, Sept. 12, 1940:

Saturated branched-chain hydrocarbons from saturated straight-chain hydrocarbons.

Double compounds of aluminum halides (aluminum chloride, aluminum bromide, aluminum iodide, and aluminum fluoride) with aromatic hydrocarbons (particularly alkylated aromatic hydrocarbons such as butylbenzene or tripropylbenzene) are used as catalysts in the isomerization of straight-chain hydrocarbons boiling below 200° C. The reaction is carried out below 150° C. in liquid or gaseous phase

(as by bubbling the hydrocarbon through the complex compound) and a hydrogen halide (hydrogen chloride or hydrogen bromide) or an organic halide (propyl chloride or *tert*-butylchloride) may be present. Examples illustrate the isomerization of *n*-pentane.

I. G. Farbenindustrie A.-G., British Patent 527,767, Oct. 16, 1940:

Isomerization of low-molecular alkanes.

Alkanes having 4-12 carbon atoms in the molecule are isomerized by being passed at temperatures between 200° and 600° C., preferably between 350° and 500° C., at pressures above 100 atmospheres, together with hydrogen having a partial pressure of less than 5 per cent of the total pressure, over catalysts having an adsorbent or hydrogenating or dehydrogenating action. Small amounts of sulfur or sulfur compounds may be added to the hydrocarbons. The catalyst may be an oxide or sulfide of metals of periodic groups 6-8; in an example it is active carbon impregnated with ammonium thiomolybdate and dried in hot carbon dioxide.

N. V. de Bataafsche Petroleum Maatschappij, British Patent 527,954, Oct. 18, 1940:

A process for preparing saturated hydrocarbons with branched, or more highly branched chains from saturated hydrocarbons.

Saturated hydrocarbons boiling below about 160° C. and having 5 or more carbon atoms are converted into isomers with more highly branched chains by treating the initial hydrocarbons with hydrogen halide under high partial pressure of hydrogen halide so as to ensure the presence of a liquid phase, in the presence of Friedel-Crafts catalysts such as aluminum chloride, tungsten chloride, molybdenum chloride, zinc chloride, ferric chloride, beryllium chloride, stannic chloride, and the like. The temperature is below 150° C. and the partial pressure of hydrogen chloride is at least one atmosphere. (Corresponds to U. S. Patent 2,250,410 and Dutch Patent 48,706.)

Anglo-Iranian Oil Co., Ltd., (S. F. Birch and J. H. Beynon), British Patent 528,178, Oct. 24, 1940:

Improvements relating to the isomerization of *n*-alkanes.

Isomerization of *n*-butane or *n*-pentane is carried out in the presence of aluminum chloride with ferric chloride as a catalyst promoter, present in amounts up to 20 per cent of the catalyst. Hydrogen chloride may be present also. Addition of 1.7 per cent of anhydrous ferric chloride to the aluminum chloride in an experiment in which *n*-butane saturated with hydrogen chloride was treated raised the conversion of *n*-butane into isobutane from 61.1 per cent to 80.24 per cent.

N. V. de Bataafsche Petroleum Maatschappij, British Patent 529,914, Dec. 2, 1940:

Hydroaromatic cyclanes.

Non-hydroaromatic cyclanes containing alkanes are heated to temperatures below 200° C. with aluminum halides in the presence of hydrogen halides and hydrogen to secure isomerization of the non-hydroaromatic cyclanes into hydroaromatic cyclanes. It is preferable to carry out the reaction at a temperature below 100° C. Aluminum halides may be employed in the form of Gustavson compounds. [*Chem. Abs.*, 35, 7414 (1941).]

N. V. de Bataafsche Petroleum Maatschappij, British Patent 530,253, Dec. 9, 1940:

Branched-chain hydrocarbons.

Unsaturated aliphatic hydrocarbons are hydrogenated. The mixture of saturated hydrocarbons and hydrogen thus produced is freed from carbon monoxide and sulfur compounds. Then it is isomerized by treatment with aluminum halides. The presence of hydrogen chloride or alkyl chlorides promotes the reaction. Gustavson's compounds, *i.e.*, double compounds of aluminum halides with aromatic hydrocarbons, may be used instead of aluminum chloride. [*Chem. Abs.*, 35, 7972 (1941).]

Standard Oil Development Co., British Patent 534,151, Feb. 28, 1941:

Converting hydrocarbons.

Straight-chain hydrocarbons are converted into branched-chain alkenes having the same number of carbon atoms by passage at 320-595° and atmospheric pressure for 5-200 seconds over dehydrogenating-isomerizing catalysts. They comprise an oxide or silicate of aluminum with or without a carrier (silica gel) which has been activated by treatment with a mineral acid (phosphoric acid, hydrogen fluoride) or by addition of a Friedel-Crafts catalyst or of an oxide and/or sulfide of a periodic group 6 metal. The catalyst may also be phosphoric acid on silica gel. [*Brit. Chem. Abs.-B*, 1941, I, 219.]

N. V. de Bataafsche Petroleum Maatschappij, British Patent 535,054, March 27, 1941:

Motor fuels.

Conversion of saturated hydrocarbons boiling below 200° C. into isomeric hydrocarbons, *e.g.*, butane into isobutane, pentane into isopentane, hexane into branched-chain hexanes, octane into branched-chain octanes, and mixtures of normal hydrocarbons of straight-run gasoline into mixtures containing branched or more highly branched hydrocarbons. Aluminum halides are employed as catalysts at temperatures not exceeding 200° C., and the formation of by-products is repressed by carrying out the reaction in the presence of hydrogen under a total operating pressure greater than atmospheric. [*J. Inst. Petroleum*, 27, 268A (1941).]

N. V. de Bataafsche Petroleum Maatschappij, British Patent 535,394, April 8, 1941:

Treatment of hydrocarbons in the liquid phase with metal halides, particularly in the isomerization of saturated hydrocarbons with straight or only slightly branched chains to hydrocarbons with branched or relatively highly branched chains. According to the invention, for example, *n*-butane can be converted into isobutane, *n*-pentane into isopentane, etc., and saturated gasolines with relatively low antiknock values into gasolines with relatively high antiknock values. [*J. Inst. Petroleum*, 27, 269A (1941).]

Standard Oil Development Co., British Patent 535,398, April 8, 1941:

Conversion of normally liquid straight-chain alkanes into branched-chain alkanes by subjecting the former to the action of a catalyst of the aluminum chloride type and an activator for the catalyst, in the presence of free hydrogen and a light alkane gas containing a substantial amount of propane. [*J. Inst. Petroleum*, 27, 269A (1941).]

Standard Oil Development Co., British Patent Application 12092/40:

Improvement relating to the isomerization of alkanes.

Liquid phase isomerization of *n*-alkanes or alkane fractions containing butane or heavier hydrocarbons at 4.4-148.9° C., space velocity of 0.1 to 5, with large amounts of catalyst present (at least equal to the hydrocarbon feed weight) and in the presence of 0.5 to 25 per cent of hydrogen chloride. Describes both fixed-bed and slurry-type operations with entrained powdered aluminum chloride. Discusses the use of hydrogen to suppress side reactions.

In the fixed-bed operation, granular aluminum chloride or a supported catalyst may be used, the supports mentioned being pumice, fuller's earth, kaolin, diatomaceous earth, "Filtrol," silica, alumina, and bauxite. In moving-bed operation, the spent catalyst is continuously removed and replaced by fresh granular catalyst fed from a hopper. Percolation-type reactors may be used singly or in groups, and the individuals comprising the latter may be used in series or in parallel, with optional temperature variations between the members, and with provision for using the first towers for purification of the feed stocks.

Canadian Patents

Shell Development Co., (assignee of A. J. van Peski and H. F. J. Lorange), Canadian Patent 384,317, Sept. 26, 1939:

Conversion of *n*-butene into isobutene.

A gaseous hydrocarbon mixture containing about 50 per cent each of butane and *n*-butenes is brought into contact with a solid catalyst

comprising a calcined mixture of a phosphorus oxy-acid and a solid siliceous material at about 275-325° for about 2-50 seconds. Polymerization of the butenes is substantially obviated. [*Chem. Abs.*, 34, 1336 (1940).]

Shell Development Co., (assignee of W. F. Engel), Canadian Patent 399,051, Sept. 2, 1941:

Hydrocarbon isomerization (7 claims).

Claim 1. A process for the conversion of normal and branched-chain saturated hydrocarbons to branched and more highly branched-chain saturated hydrocarbons which comprises contacting the hydrocarbon to be treated at a temperature not greater than 200° C. with a solid catalyst essentially comprising an effective amount of anhydrous aluminum chloride and an aluminum oxide which has been previously partially dehydrated by a heat treatment at a temperature greater than 200° C. until it is capable of losing further water of hydration at higher temperatures, but is incapable of further substantial dehydration at a temperature below 200° C. [Canadian Patent Office Record, 69, 2451 (1941).]

Dutch Patents

N. V. de Bataafsche Petroleum Maatschappij, Dutch Patent 48,338, April 15, 1940 (Application 87,201 of April 1, 1938):

Producing isoalkanes from *n*-alkanes.

Isoalkanes are produced from *n*-alkanes boiling below 100° C. by treatment with aluminum halides in the form of double compounds of aluminum halide and aromatics containing one or more alkyl groups. The temperature is below 150° C., generally room temperature, and hydrogen halide or an organic halide is added. *n*-Butane is converted into isobutane, *n*-pentane into isopentane, or a mixture of normal hydrocarbons boiling below 100° C. (e.g., fractions of straight-run gasolines) into a mixture of branched-chain hydrocarbons. Reaction may be effected in either liquid or in vapor phase, and, if desired, increased pressure may be applied.

N. V. de Bataafsche Petroleum Maatschappij, (assignee of H. Hoog), Dutch Patent 48,509, May 15, 1940:

See British Patent 501,896 of March 7, 1939, and French Patent 841,004 of May 9, 1939.

N. V. de Bataafsche Petroleum Maatschappij, Dutch Patent 48,706, June 15, 1940:

Isomerization of alkanes.

Saturated straight-chain hydrocarbons containing 5 or more carbon atoms, with b.p. of 160° or less, are converted into branched-

chain saturated hydrocarbons by treatment with hydrogen halide under sufficient pressure to cause a liquid phase to be present and in the presence of Friedel-Crafts type of catalyzers. The conversion is effected at temperatures below 150° and with a partial pressure of hydrogen halide of at least one atmosphere. Especially suggested is the use of aluminum chloride and hydrogen chloride at temperatures below 100° . [*Chem. Abs.*, 35, 1412 (1941). Cf. British Patent 527,954 and U. S. Patent 2,250,410.]

N. V. de Bataafsche Petroleum Maatschappij, Dutch Patent 50,385, May 15, 1941 (Application 89,775 of Sept. 16, 1938):

Isomerization of *n*-butane and *n*-pentane.

n-Butane or pentane is treated in the liquid phase below 200° with aluminum halide or mixtures such as aluminum chloride and *tert*-butyl chloride in the presence of hydrogen under pressure. Too high a hydrogen pressure (*e.g.*, 200 atmospheres) with pentane at 40° will prevent isomerization. [*Chem. Abs.*, 35, 7700 (1941).]

N. V. de Bataafsche Petroleum Maatschappij, Dutch Application 83,778, Aug. 14, 1937 (Filed), Aug. 15, 1939 (Laid open):

Producing branched alkenes from *n*-alkenes.

Branched-chain alkenes are produced from *n*-alkenes by contact at elevated temperature (275 - 500° C.) with hydrated aluminum silicates of the permutite or zeolite type, particularly with hydrated alkaline aluminum silicate. The process is especially suitable for conversion of butane-butene mixtures. The process can be carried out under pressure, but care should be taken not to cause undesirable polymerization by too great a pressure. The lower alkenes such as butene-1 or butene-2 can be treated at higher temperatures and during a longer contact time than the higher alkenes, without danger of cracking or dehydrogenation.

N. V. de Bataafsche Petroleum Maatschappij, Dutch Application 83,820, Aug. 18, 1937 (Filed), May 15, 1940 (Opp. expired):

Isobutane from *n*-butane.

Isobutane is prepared from *n*-butane by treating the latter below 200° C., with a Friedel-Crafts type halide catalyst, such as aluminum chloride or aluminum bromide. The contact time is short enough so that isomerization is the chief reaction taking place.

N. V. de Bataafsche Petroleum Maatschappij, Dutch Application 86,418, Feb. 12, 1938 (Filed), May 15, 1940 (Opp. expired):

Isobutane from *n*-butane.

n-Butane or mixtures containing it are treated at temperatures below 200° C. with mixtures of aluminum chloride and inorganic substances that contain water normally driven off by heating to over 200° C. (*e.g.*, china clay dried at 300° C.). Atmospheric, reduced, or

elevated pressure may be used, and either liquid- or gas-phase reaction is permissible.

N. V. de Bataafsche Maatschappij, Dutch Application 87,959, May 21, 1938 (Filed), May 15, 1940 (Opp. expired):

Isomerization of alkanes.

Corresponds to French Patent 854,936 of April 27, 1940 (Published).

French Patents

Badische Anilin- und Soda-Fabrik, French Patent 17,235, Feb. 19, 1913: Isoprene.

Addition to French Patent 440,130 of Feb. 13, 1912. Instead of 3-methylbutadiene-1,2, the 3-methylbutyne-1 may be used for making isoprene. (*Chem. Abs.*, 8, 1022 (1914); corresponds to German Patent 268,102 of Dec. 8, 1913.

Standard Oil Development Co., French Patent 837,202, Feb. 6, 1939:

Hydrocarbons for use as motor fuel.

Unsaturated hydrocarbons of low boiling point composed mainly of *n*-alkenes are subjected to heating in the presence of isomerizing and polymerizing catalysts. Sulfuric acid may be used as catalyst and may be in the form of 60-80 per cent solution. Reaction may be effected at 77-163° C. and at elevated pressure. [*Chem. Abs.*, 33, 7091 (1939).]

Texas Development Corp., French Patent 840,717, May 3, 1939:

Alkylated hydrocarbons.

Motor fuels of high antiknock value are prepared by transforming *n*-butane, by isomerization in the presence of aluminum halide, into isobutane and causing this to react with an alkene in the presence of a mineral acid (sulfuric acid) which gives an isoalkane of higher molecular weight than the alkene (butenes). [*Chem. Abs.*, 33, 8983 (1939).]

N. V. de Bataafsche Petroleum Maatschappij, French Patent 852,114, Jan. 24, 1940 (Published):

Isoalkanes from *n*-alkanes.

Branched alkanes are prepared from straight-chain or less branched alkanes by treatment at temperatures below 150° C. in the presence of double compounds of aluminum halide with aromatic hydrocarbons, preferably alkylated aromatic hydrocarbons, in the presence of a hydrogen halide or an organic halide.

N. V. de Bataafsche Petroleum Maatschappij, French Patent 854,936, Jan. 29, 1940 (Issued), April 27, 1940 (Published):

Branched-chain from straight-chain hydrocarbons.

Saturated hydrocarbons boiling below 160° C. containing 5 or

more carbon atoms are treated at temperatures below about 150° C. (preferably below 100° C.) in the presence of Friedel-Crafts catalysts (preferably aluminum chloride) and under a partial pressure of hydrohalogen acid (hydrogen chloride) of at least one atmosphere. Pressure used is sufficient to keep the reaction in the liquid phase. The process is preferably carried out in the absence of water, and the Friedel-Crafts catalysts used are chlorides of Al, W, Mo, Zn, Fe⁺⁺⁺, Be, and Sn⁺⁺⁺⁺.

German Patents

Schering-Kahlbaum A.-G., (assignee of F. Ulffers), German Patent 596,820, May 14, 1934:

Terpenes.

In transforming terpenes, catalysts consisting of organic or inorganic acids not forming stable addition products with terpenes, or their anhydrides or salts with volatile bases, are used. Thus (NH₄)₂WO₄ is heated to 295° with superheated steam to form a suitable catalyst.

[*Chem. Abs.*, 28, 5076 (1934).]

I. G. Farbenindustrie A.-G., German Application J. 61,782, (Laid open) Aug. 10, 1939:

Catalysts for hydrocarbon reactions.

Process for carrying out catalytic reactions using as catalysts metal sulfides completely free of oxygen, produced by treatment of metal sulfides of any origin with sulfur or oxygen-free volatile sulfur compounds. The catalysts may be sulfides of metals of the second to the eighth group, used alone, in admixture, or on carriers such as activated carbon, activated silica gel, clays, bauxite, pumice, magnesite, magnesia, chromia and the like. These catalysts are suitable for hydrogenation, cracking, decomposition of original sulfur compounds in gases to be purified, isomerization of gasoline, etc.

Hungarian Application

N. V. de Bataafsche Petroleum Maatschappij, Hungarian Application P. 9,689, (Filed) July 27, 1939, (Opp. expired) May 2, 1940:

Saturated hydrocarbons boiling below 200° C., preferably those containing 4-6 carbon atoms are converted into saturated hydrocarbons with branched chains or more highly branched chains, by treatment with aluminum halides at temperatures below 200° C. in the presence of enough hydrogen to suppress decomposition. Claim 3 specifies the presence of an activating substance such as hydrogen chloride or an alkyl halide. The hydrogen may be formed in the reaction by the action of hydrogen chloride on metals. The aluminum halide may be formed wholly or partly under the reaction conditions

by the interaction of hydrogen chloride and aluminum. The process may be operated continuously by passing vaporous or gaseous hydrocarbons over the catalyst.

Italian Patent

Texaco Development Corp., Italian Patent 365,253, July 19, 1938:

Alkylated hydrocarbons.

Higher molecular weight isoalkanes, particularly antiknock gasolines, are obtained from normal hydrocarbons by conversion into isoalkanes and alkylation with alkenes. For example, *n*-butane is isomerized to isobutane with halides of aluminum, chromium or iron, especially with aluminum chloride or bromide. The isobutane is alkylated to isoöctane with butenes (*e.g.*, isobutene), diisobutene, cracked gases, liquid cracked distillates or polymer gasolines, in the presence of a mineral acid (phosphoric acid or 80-100 per cent sulfuric acid) at temperatures between -17° and $+205^{\circ}$ C., particularly at $21-38^{\circ}$. Corresponds to French Patent 840,717 of May 3, 1939. [*Oel u. Kohle ver. Petroleum*, 36, S-26 (1940).]

Russian Patent

A. V. Frost, E. K. Serebriakova and D. M. Rudkovsky, Russian Patent 51,181, June 30, 1937:

Isomerization of alkenes.

Alkenes are heated to $200-400^{\circ}$ C. in the presence of phosphoric acid, acid sulfates or phosphates of metals of the first, second, or third groups of the periodic system, or of Fe, Co, Ni, Cr, and Mn as catalysts, which may be supported on carriers. Gases or vapors may be added advantageously to the alkenes to prevent polymerization. A mixture of *n*-butenes with 2-4 per cent of isobutene soluble in 68 per cent sulfuric acid, is passed at $200-400^{\circ}$ C. over chamotte impregnated with phosphoric acid. The reaction product contains 15-40 per cent of isobutene soluble in 68 per cent sulfuric acid [*Chem. Zentr.*, 1938, II, 592].

U. S. Patents

H. Meerwein, F. Ulffers, R. Erbe, F. Aichner, and W. Klaphake, (assignors to Schering-Kahlbaum A.-G.), U. S. Patent 1,985,792, Dec. 25, 1934:

Catalysts for conversion of terpenes, such as in producing camphene from nopinene and α -pinene.

A base such as sodium hydroxide or ammonia is caused to react with an inorganic acid, inorganic "complex" inorganic acid or inorganic-organic "complex" acid such as tungstic acid or phosphotungstic

acid which combines with terpenes, if at all, only "reluctantly" or with a salt of such an acid which has an acid reaction and the base is subsequently removed from the salt formed (as by acid or evaporation) and the product is converted into a hydrate of high catalytic efficiency. Numerous examples are given. [*Chem. Abs.*, 29, 1104 (1935).]

A. J. van Peski, (assignor to Shell Development Co.), U. S. Patent 2,105,850, Jan. 18, 1938:

Process for the reforming of gasoline distillate (11 claims).

Claim 1. In the process of reforming gasoline distillates to improve their antiknock rating, the steps comprising contacting a gasoline distillate of low antiknock rating at a reforming temperature between 225° and 500° C. with a reforming catalyst in the presence of a small quantity of a tertiary alkyl halide for a time sufficient to effect reforming without forming a substantial amount of gas.

E. M. Marks, (assignor to Atlantic Refining Co.), U. S. Patent 2,164,334, July 4, 1939:

Antiknock motor fuel.

Gasoline of high antiknock value is produced by chlorinating naphtha having a relatively low antiknock value to produce chlorinated naphtha containing about 5-20 per cent of chlorine, heating the chlorinated naphtha to about 200-450° C. under substantial superatmospheric pressure to isomerize it, then heating at substantially atmospheric pressure to about 200-240° C. in the presence of a dechlorinating agent.

E. A. Ocon, U. S. Patent 2,175,359, Oct. 10, 1939:

Reducing and recovering branched chain aliphatics.

The straight-chain aliphatic hydrocarbons that occur in natural gas and crude petroleum, or the oxygenated derivatives of these hydrocarbons are transformed to branched chain aliphatics by a multistage process. Oxygenated derivatives such as alcohols produced by treating cracking gas with concentrated sulfuric acid at 32.2° C., to remove mainly isoalkenes and hydrolyzing, are passed with suitable proportions of reducing gas (*e.g.*, water gas or water gas enriched with hydrogen) over a catalyst with relatively high hydrogenating and low dehydrating activity, at 315.6-482.2° C. at superatmospheric pressure, with a space velocity of 75-200 cu. ft. per hr. per cu. ft. of catalyst. The catalyst may be zinc oxide, chromia, cuprous oxide, manganous oxide, etc., singly or mixed, and in the presence of an alkaline compound (potassium carbonate, potassium hydroxide, alkali salts of aliphatic acids and the like), and may be on an inert carrier. Suggested catalyst mixtures are cobalt-alumina; molybdena-alumina, etc.; it is best to avoid a catalyst with too strong hydrogenating tendencies, such as nickel. Products from the *hydro-isomerization zone*

are fractionated into an overhead of low-boiling hydrocarbons, and a reflux containing unconverted alcohols. A heavy unvaporized hydrocarbon fraction may be removed from the catalytic zone. The low-boiling iso-aliphatics may be hydrogenated or polymerized for aviation fuel ingredients. Similar to British Patent 535,210, April 2, 1941 (E. A. Ocon).

M. M. Holm and W. H. Shiffler, (assignors to Standard Oil Co. of California), U. S. Patent 2,186,022, Jan. 9, 1940:

A catalyst of character similar to U. S. Patent 2,186,021 (comprising a thin film of active polymerizing agent such as phosphoric acid carried on the surface of particles of a nonporous inert solid such as quartz) is used to effect reactions such as isomerization, without polymerization. [*Chem. Abs.*, 34, 2862 (1940).]

C. M. Hull, (assignor to Standard Oil Co. of Indiana), U. S. Patent 2,199,132, Apr. 30, 1940:

Catalytic process comprising polymerization, isomerization and dehydrogenation.

The patent relates to a process for converting C_4 hydrocarbons resulting from a cracking operation into motor fuel. The hydrocarbons are first polymerized using phosphoric acid catalyst to convert the butenes. The *n*-butane stream is then catalytically isomerized using an aluminum halide-hydrogen halide catalyst. The isobutane formed is treated with a dehydrogenating catalyst and the isobutene formed recycled to the polymerization step. The polymers formed are hydrogenated to produce octanes.

M. Pier and K. Schoenemann, (assignors to I. G. Farbenindustrie A.-G.), U. S. Patent 2,216,131, Oct. 1, 1940:

Polynuclear carbon compounds.

A bituminous material is heated under pressure with hydrogen to effect substantial hydrogenation and formation of substantial amounts of polynuclear carbon compounds and cyclic carbon compounds of the hydroaromatic series, and the fraction of the product that contains the polynuclear and cyclic compounds is heated in the presence of an isomerization catalyst to effect isomerization of the polynuclear and cyclic compounds. [*Chem. Abs.*, 35, 753 (1941).]

C. L. Thomas and H. S. Bloch, (assignors to Universal Oil Products Co.), U. S. Patent 2,216,285, Oct. 1, 1940:

Isomerization of *n*-Butene (8 claims).

A process for converting *n*-butenes into isobutene which comprises contacting said *n*-butenes with a synthetically prepared composite mass of silica, alumina, and thoria at a temperature in the approximate range of 371-593° C. Results obtained at 450-505° C. are disclosed, indicating up to 20.5 per cent isomerization of the *n*-butenes.

W. E. Forney, (assignor to Power Patents Co.), U. S. Patent 2,216,470, Oct. 1, 1940:

Catalytic conversion of natural gas gasoline, etc., to obtain improved antiknock character.

An arrangement of apparatus is described, and a process of catalytically converting an alkane containing from 3 to 4 carbon atoms to the molecule into a mixture of hydrocarbons having a substantially higher molecular weight, which comprises carrying out the process in the absence of added hydrocarbons of other type and hydrogen at a superatmospheric pressure of from 27.22 to 40.83 atmospheres, pre-heating the aliphatic hydrocarbon to be converted and mixing it with a relatively small proportion of a solid catalytic metallic salt which is adapted to catalyze isomerization and alkylation reactions, passing the resulting mixture in a stream of restricted cross-section through a long heating zone in the first part of which the mixture is heated to at least 398.9° C. and in the latter part of which the temperature is substantially maintained and raised to approximately 454.4° C., discharging the resulting heated mixture into an enlarged reaction zone in which intimate contact is maintained between the hydrocarbons and the catalytic material, passing the mixture into a separator in which the catalytic material is separated from the resulting converted hydrocarbon, and recovering the condensable products resulting from the conversion reactions. Catalytic salts used may be the Fe, Al, Cu, Zn, Mo, Cr, Mn, or Ni salts of phosphoric, sulfuric, hydrochloric, silicic, or boric acids. [*Chem. Abs.*, 35, 1215 (1941).]

B. L. Evering and G. G. Lamb [assignors to Standard Oil Co. (Indiana)], U. S. Patent 2,220,090, Nov. 5, 1940:

Conversion of hydrocarbon products (6 claims).

In a process for converting substantial amounts of the straight-chain alkanes in a low antiknock straight run petroleum naphtha into saturated branched-chain hydrocarbons whereby a motor fuel fraction having a relatively high antiknock value is obtained, the steps comprising contacting in a reaction zone an admixture of said petroleum naphtha, isobutane, a conversion catalyst selected from the group consisting of aluminum chloride, aluminum bromide and their hydrocarbon complexes, and a halogen-containing promoter for said catalyst, the reacting hydrocarbon gases present being largely isobutane and substantially free of unsaturated hydrocarbons, at an elevated temperature and pressure sufficient to convert a substantial part of the straight-chain alkanes in said petroleum naphtha into saturated branched-chain hydrocarbons without substantial formation of hydrogen and methane, withdrawing the products from said reaction zone and separating said motor fuel fraction from said products.

B. L. Evering and G. G. Lamb [assignors to Standard Oil Co. (Indiana)],
U. S. Patent 2,220,091, Nov. 5, 1940:

Conversion of hydrocarbon products (7 claims).

In a process for converting substantial amounts of the straight-chain alkanes in a low antiknock straight run petroleum naphtha into saturated branched-chain hydrocarbons, whereby a motor fuel fraction having a relatively high antiknock value is obtained, the steps comprising contacting in a reaction zone an admixture of said petroleum naphtha, propane, a conversion catalyst selected from the group consisting of aluminum chloride, aluminum bromide and their hydrocarbon complexes, and a halogen-containing promoter for said catalyst, the reacting hydrocarbon gases present being largely propane and substantially free of unsaturated hydrocarbons, at an elevated temperature and pressure sufficient to convert a substantial part of the straight-chain alkanes in said petroleum naphtha into saturated branched-chain hydrocarbons without substantial formation of hydrogen and methane, withdrawing the products from said reaction zone and separating said motor fuel fraction from said products.

B. L. Evering and G. G. Lamb [assignors to Standard Oil Co. (Indiana)],
U. S. Patent 2,220,092, Nov. 5, 1940:

Conversion of hydrocarbon products (8 claims).

In a process for converting substantial amounts of the straight-chain alkanes in a low antiknock straight run petroleum naphtha into saturated branched-chain hydrocarbons whereby a motor fuel fraction having a relatively high antiknock value is obtained, the step comprising contacting in a reaction zone an admixture of said petroleum naphtha, at least one normally gaseous hydrocarbon having at least two carbon atoms per molecule, a conversion catalyst selected from the group consisting of aluminum chloride, aluminum bromide and their hydrocarbon complexes, and a halogen-containing promoter for said catalyst, the reacting hydrocarbon gases present being largely heavier than methane and substantially free of unsaturated hydrocarbons, at an elevated temperature and pressure sufficient to convert a substantial part of the straight-chain alkanes in said petroleum naphtha into saturated branched-chain hydrocarbons without substantial formation of hydrogen and methane, withdrawing the products from said reaction zone and separating said motor fuel fraction from said products.

L. C. Kemp (assignor to The Texas Co.), U. S. Patent 2,238,860, April 15, 1941:

Motor fuel.

An arrangement of apparatus is described, and a process for the conversion of natural gasoline hydrocarbons into high-octane motor fuel

hydrocarbons which involves fractionating natural gasoline to separate therefrom fractions respectively rich in *n*-butane and isobutane and to produce a fraction comprising mainly hydrocarbons of higher molecular weight than butane, subjecting the *n*-butane fraction to isomerization to produce isobutane, subjecting the fraction comprising hydrocarbons of higher molecular weight than butane to thermal conversion to form alkenes including normally gaseous alkenes, fractionating the products of conversion to separate therefrom a fraction comprising C₃ and C₄ hydrocarbons, including alkenes, and a high-boiling fraction comprising motor-fuel hydrocarbons of relatively high octane rating, subjecting the C₃ and C₄ fraction to alkylation with the isobutane, and subjecting the products of alkylation to fractionation to separate therefrom a fraction comprising hydrocarbons suitable as aviation motor fuel of high octane value. [*Chem. Abs.*, 35, 5300 (1941).]

A. J. van Peski and G. H. Visser (assignors to Shell Development Co.), U. S. Patent 2,249,366, July 15, 1941:

Production of isobutane.

n-Butane is treated with aluminum halide (aluminum chloride or aluminum bromide) and hydrogen halide in the presence of at least 3 atmospheres pressure of hydrogen halide and temperatures of 60-120° C. when vapor phase isomerization is carried out, or at temperatures below 100° C. when the butane is treated in the liquid phase. The catalyst may be employed in either solid or liquid phase.

W. C. B. Smithuysen (assignor to Shell Development Co.), U. S. Patent 2,250,118, July 22, 1941:

Isomerization of hydrocarbons.

Isomerization of normal saturated hydrocarbons with 4 to 9 carbon atoms by contacting at 20-140° C. with a preformed complex compound of aluminum halide (aluminum chloride) and an alkylated aromatic hydrocarbon, in the presence of hydrogen halide (hydrogen chloride). (Corresponds to Dutch Patent 48,338 and French Patent 852,114).

A. J. van Peski (assignor to Shell Development Co.), U. S. Patent 2,250,410, July 22, 1941:

Catalytic treatment of hydrocarbons.

A normally liquid *n*-alkane with at least 5 carbon atoms per molecule, and boiling not above 160° C. is converted into the isoalkane by contact at 20-150° C. with an acid-acting halide catalyst (halides of Al, Zn, Fe, As, Sb, Mo, W, etc.) for a time not exceeding 17 hours under a pressure of hydrogen halide equivalent to 3-20 atmospheres when measured at 20° C. (Corresponds to British Patent 527,954 and Dutch Patent 48,706).

W. A. Yarnall (assignor to The Texas Co.), U. S. Patent 2,257,896, Oct. 7, 1941:

Catalytic treatment of hydrocarbons.

Petroleum hydrocarbons, particularly gaseous alkanes such as *n*-butane, are isomerized by treating them with a solution of a non-gaseous halide of polyvalent metal or metalloid in anhydrous liquefied hydrogen halide under pressure higher than the vapor pressure of the hydrogen halide at the temperature of treatment to maintain liquid conditions. The metal or metalloid halides mentioned are those of Be, B, Al, Si, P, S, Ti, V, Cr, Fe, Ni, Co, Cu, Zn, Ga, Ge, As, Se, Zr, Mo, Ag, Cd, In, Sn, Sb, Te, Ce, Ta, W, Hg, Pb, Bi, and U. *n*-Butane is converted into isobutane at -1.11 to $+51.7^{\circ}$ C. using aluminum chloride dissolved in hydrogen halide.

E. L. d'Ouville, B. L. Evering, and A. G. Oblad [assignors to Standard Oil Co. (Indiana)], U. S. Patent 2,260,279, Oct. 21, 1941:

Branched-chain hydrocarbons from hydrocarbon mixtures.

Effective conversion of *n*-alkanes into isoalkanes by treatment with aluminum chloride requires a feed stock substantially free of aromatics. A mixture of alkanes with naphthenes and/or aromatics, such as a naphtha, is subjected first to an aromatization step if it contains naphthenes, to convert the latter into aromatics, next to an extraction to selectively remove the aromatics so that the stock contains not more than 2 volume per cent of aromatics, and the raffinate is isomerized. The aromatization step may be carried out at 260 - 537.8° C., preferably 454.4° C., under hydrogen pressure over suitable catalysts (for example, $90 \text{ Al}_2\text{O}_3:10 \text{ Cr}_2\text{O}_3$); hydrogen is removed in a gas separator, and the gas-free stock is extracted with a selective solvent which may be liquefied sulfur dioxide, an aluminum chloride-hydrocarbon complex, or other solvents; the raffinate is isomerized with aluminum halide catalyst in the presence of an activator (suitably aluminum chloride with hydrogen chloride), or with aluminum chloride-hydrocarbon complex. In the isomerization step hydrogen may be introduced. The removal of aromatics may be effected by alkylation with low molecular weight alkenes, followed by distillation, instead of using solvent extraction. The broadest claims cover treating a naphtha containing straight-chain alkanes and aromatics to give a mixture containing alkanes and not more than 2 per cent of aromatics and subjecting this to isomerization with aluminum halide and an activator yielding hydrogen halide.

M. H. Arveson [assignor to Standard Oil Co. (Indiana)], U. S. Patent 2,263,026, Nov. 18, 1941:

Combination dehydrogenation and isomerization process.

This patent relates to a process which comprises subjecting alkane-

containing gasoline to the action of a dehydrogenation catalyst at a temperature of about 398.9 to 482.2° C. and then conducting the alkenes and hydrogen vapors from said step to a second zone wherein the alkenes undergo isomerization in the presence of a catalyst comprising phosphoric acid or aluminum oxide. The dehydrogenation catalyst may comprise an oxide of chromium or of molybdenum.

The claims cover the catalysts mentioned and reaction pressures of about 0.68 to 3.4 atmospheres.

G. C. A. Schuit (assignor to Shell Development Co.), U. S. Patent 2,265,548, Dec. 9, 1941:

Process for the production of isobutane (8 claims).

Claim 1. In a process for the production of isobutane by the catalytic isomerization of *n*-butane wherein the isomerization is effected by contacting *n*-butane with an aluminum halide isomerization catalyst and a hydrogen halide promoter under isomerization conditions to effect the isomerization of *n*-butane as the predominant reaction, the improvement which comprises effecting the isomerization in the presence of an aluminum halide catalyst containing a metal which reacts with a portion of the hydrogen halide promoter, whereby undesirable side reactions are repressed.

G. C. A. Schuit (assignor to Shell Development Co.), U. S. Patent 2,265,870, Dec. 9, 1941:

Isomerization of hydrocarbons (9 claims).

Claim 1. In a process for the isomerization of hydrocarbons wherein a saturated hydrocarbon containing at least five carbon atoms is contacted with an aluminum chloride isomerization catalyst and a hydrogen halide promoter under isomerization conditions to effect isomerization as the predominant reaction, the improvement which comprises effecting the isomerization in the presence of an aluminum chloride catalyst containing sufficient metallic aluminum to react with a portion of the hydrogen halide promoter, whereby undesirable side reactions are repressed.

E. L. d'Ouille and B. L. Evering [assignors to Standard Oil Co. (Indiana)], U. S. Patent 2,266,011, Dec. 16, 1941:

Production of isobutane from *n*-butane (11 claims).

This patent relates to the production of isobutane by contacting a mixture of propane, *n*-butane, and an aluminum halide catalyst at a temperature of about 121.1° to 287.8° C., preferably 176.7° to 246.1° C., and a pressure of about 34.0 to 408.3 atmospheres, with the addition of an activator which may be a hydrogen halide or a compound yielding hydrogen halide under the reaction conditions.

In the isomerization of *n*-butane by treatment with an aluminum halide catalyst effective in converting *n*-butane into isobutane and

an activator for said catalyst at a temperature in the range from about 121.1° C. to about 287.8° C., the improvement which comprises carrying out said treatment in the presence of about 10 to 50 per cent of propane by weight based on the *n*-butane undergoing treatment.

E. L. d'Ouille and B. L. Evering [assignors to Standard Oil Co. (Indiana)], U. S. Patent 2,266,012, Dec. 16, 1941:

Production of branched-chain alkanes (14 claims).

This patent relates to the production of branched-chain alkanes from normally liquid hydrocarbons and more particularly to the conversion of normally liquid saturated hydrocarbons and mixtures thereof containing a large proportion of straight-chain alkanes into products consisting predominantly of branched-chain alkanes.

The process of converting a substantial portion of the straight-chain alkanes in a substantially saturated normally liquid hydrocarbon fraction into branched-chain alkanes which comprises contacting an admixture of said hydrocarbon fraction, an aluminum halide catalyst effective in causing said conversion, an activator for said catalyst, free hydrogen and an alkane gas containing a substantial amount of propane in a reaction zone maintained at a temperature in the range from about 148.9° C. to about 287.8° C. and a pressure in the range from about 34.0 to 408.3 atmospheres, said propane being present in said reaction zone in an amount lying in the range from about 10 per cent to about 35 per cent by weight based on the straight-chain alkanes present.

C. N. Kimberlin, Jr. (assignor to Standard Oil Development Co.), U. S. Patent 2,268,401, Dec. 30, 1941:

Isomerization process (3 claims).

A process for isomerizing alkanes in the presence of a Friedel-Crafts type catalyst (aluminum chloride) and a hydrogen halide (hydrogen chloride) as activator. Small amounts of an alkyl halide (carbon tetrachloride) are added to the reaction mixture as required to make up for losses of the catalyst activator during the process.

A. J. van Peski (assignor to Shell Development Co.), U. S. Patent 2,271,043, Jan. 27, 1942:

Isomerization of hydrocarbons (9 claims).

This invention relates particularly to the catalytic conversion of *n*-butane and *n*-pentane into isobutane and isopentane, respectively. Nine examples are submitted to illustrate various aspects of the invention.

"The isomerization is preferably effected with the aid of an aluminum halide such as aluminum chloride or aluminum bromide. Although the aluminum halides are, in general, the most practical and efficient catalysts, such other acid-acting halide catalysts as exert a

catálytic influence on the isomerization of hydrocarbons, *e.g.*, the halides of Be, Zn, Zr, Nb, Ta, Sb, and B, may also, if desired, be employed. Exceptionally suitable catalyst combinations are mixtures of an aluminum halide with a free metal of the group consisting of Al, Be, Mg, Zn, Cu, and Fe.

"The catalysts are preferably employed in the solid state in any suitable form such as granules, powder, or pellets of the desired size, preferably deposited on or mixed with a suitable solid supporting material. Particularly effective catalysts are produced when aluminum chloride is supported in or intimately mixed with one of the various siliceous and/or aluminous materials of natural or synthetic origin which contain an appreciable amount of firmly-bound water. Suitable materials of the category are, for example, the naturally-occurring minerals and clays, such as pipe clay, bauxite, fuller's earth, bentonite, kaolin, Florida earth, meerschaum, infusorial earth, kieselguhr, diatomaceous earth, montmorillonite, the permutites, and the like; the various treated clays and clay-like materials, such as Tonsil, Celite, Sil-O-Cel, Terrana and the like; and artificially prepared materials, such as Activated Alumina, silica gel, the artificial permutites, and the like. The aluminum halide may, moreover, be simply suspended in the liquid reaction mixture, or it may be employed in the form of a complex double compound such, for instance, as those known as "Gustavson's compounds" (C. 1903, II, 1113) and the "Ansolve Acids" (*Ann.*, 455, 227-253).

"The isomerization is executed, according to the process of the present invention, under a pressure of hydrogen. It is found that hydrogen exerts a remarkable and unexpected influence in the isomerization reaction and that an appreciable pressure of hydrogen is, in general, very beneficial. By the use of suitable pressure of hydrogen, higher temperatures affording more practical reaction rates may be employed, undesirable side reactions are repressed, and the active life of the catalyst is materially increased.

"It is also found that moderate hydrogen pressures, *i.e.*, from about one to about five atmospheres (measured at 20° C.), tend to a certain extent to promote the isomerizing activity of the catalyst. Thus, whereas unpromoted aluminum halides are known not to catalyze isomerization to any appreciable extent, it is found that, in the case of the isomerization of normal butane and normal pentane, the isomerization may be effected even in the absence of a hydrogen halide if a suitable pressure of hydrogen is applied."

Bibliography

1. Abell, R. D., *J. Chem. Soc.*, **83**, 367-374 (1903).
2. Agejewa, M., *J. Russ. Phys.-Chem. Soc.*, **37**, 662-668 (1905); *Chem. Zentr.*, 1905, II, 1017.
- 2a. Alder, K., and Windemuth, E., *Ann.*, **543**, 41-56 (1940).
- 2b. —, —, *Ann.*, **543**, 56-78 (1940).
3. Althausen, D., and Marvel, C. S., *J. Am. Chem. Soc.*, **54**, 1174-1184 (1932).
- 3a. Andant, A., Lambert, P., and Lecomte, J., *Compt. rend.*, **198**, 1316-1317 (1934).
4. Ando, S., *J. Soc. Chem. Ind. Japan (Supplement)*, **42**, 322B-324B (1939).
5. —, *Ibid.*, **42**, 391B-393B (1939).
- 5a. —, *Ibid.*, **43**, 328B-330B (1940).
- 5b. —, *Ibid.*, **43**, 355B-356B (1940).
- 5c. Anglo-Iranian Oil Co., Ltd., Humble Oil and Refining Co., Shell Development Co., Standard Oil Development Co., and the Texas Co., Am. Petroleum Inst., Chicago Meeting, Nov. 13-17, 1939; *Oil Gas J.*, **38**, No. 27, 104-108 (1939).
6. Anschütz, R., *Ann.*, **235**, 150-229 (1886).
7. —, and Immendorff, H., *Ber.*, **18**, 657-662 (1885).
8. Arbusov, B. A., *Ber.*, **67B**, 563-569 (1934).
9. —, *Ber.*, **67B**, 569-573 (1934).
10. —, *J. Gen. Chem. (U.S.S.R.)*, **3**, 21-27, 28-34 (1933).
11. —, *Ibid.*, **6**, 206-216, 217-226 (1936).
12. —, *Ibid.*, **6**, 297-299 (1936); *Trans. Kirov Inst. Chem. Tech. Kazan*, 1935, No. 4-5, 53-56.
- 12a. Arbusov, J. A., and Zelinsky, N. D., *Compt. rend. acad. sci. U.R.S.S.*, **30**, 717-720 (1941) (in English).
- 12b. —, —, *Ibid.*, **30**, 721-722 (1941) (in English).
13. Armstrong, H. E., and Tilden, W. A., *Ber.*, **12**, 1752-1756 (1879).
14. —, —, *J. Chem. Soc.*, **35**, 733T-759T (1879).
15. Arrhenius, S., *Z. physik. Chem.*, **4**, 226-248 (1889).
- 15a. Asahina, Y., and Ishidate, M., *Ber.*, **68B**, 555-558 (1935).
- 15b. —, —, and Sano, T., *Ber.*, **69B**, 343-348 (1936).
16. Aschan, O., *Ann.*, **324**, 1-39 (1902).
17. —, *Översikt Finska Vetenskaps-Soc. Förh.*, **57**, Part A, No. 1, 35 pp. (1914); *Chem. Zentr.*, 1921, III, 629-631.
- 17a. Aston, J. G., *Chem. Rev.*, **27**, 59-73 (1940).
18. Austerweil, G., British Patent 258,901, Nov. 17, 1926; French Patent 621,954, May 20, 1927; *Chem. Zentr.*, 1927, II, 2116.
19. —, *Bull. soc. chim. (4)*, **39**, 690-698 (1926).
20. —, *Ibid.*, **39**, 1643-1646 (1926).
21. —, and Petrovici, O., *Ibid.*, **39**, 1732-1744 (1926).
22. Auwers, K. von, and Müller, K., *Ber.*, **44**, 1595-1608 (1911).
23. —, and Ziegler, K., *Ann.*, **425**, 217-280 (1921).
24. Bachman, G. B., and Hill, A. J., *J. Am. Chem. Soc.*, **56**, 2730-2732 (1934).
25. Bachmann, W. E., Cook, J. W., Hewett, C. L., and Iball, J., *J. Chem. Soc.*, 1936, 54-61.
26. —, and Kloetzel, M. C., *J. Am. Chem. Soc.*, **59**, 2207-2213 (1937).
27. Baddeley, G., and Kenner, J., *J. Chem. Soc.*, 1935, 303-309.
28. —, —, *Ber.*, **69B**, 902-904 (1936).
29. Badische Anilin- und Soda-Fabrik, British Patent 976, Jan. 13, 1913.
30. —, French Patent 440,130, Feb. 13, 1912.
31. —, German Patent 251,216, May 17, 1912; Friedlaender's *Fortschritte der Teerfarbenfabrikation*, **10**, 1038 (1913).
32. —, German Patent 268,102, Aug. 28, 1913; *Ibid.*, **11**, 811-812 (1915).
33. —, German Patent 263,017, June 1, 1912; *Ibid.*, **11**, 810-811 (1915); U. S. Patent 1,102,655, July 7, 1914.
34. Badoche, M., *Bull. soc. chim. (5)*, **5**, 164-169 (1938).
35. Barbier, P., and Grignard, V., *Bull. soc. chim. (4)*, **5**, 512-519 (1909).
36. —, —, *Ibid.*, **5**, 519-526 (1909).
37. Barrett, J. W., and Linstead, R. P., *J. Chem. Soc.*, 1936, 611-616.
- 37a. Bartlett, J. H., (assignor to Standard Oil Development Co.), U. S. Patent 2,216,221, Oct. 21, 1940.
38. Bartlett, P. D., and Pöckel, I., *J. Am. Chem. Soc.*, **59**, 820-825 (1937).
39. —, —, *Ibid.*, **60**, 1585-1590 (1938).
- 39a. Bauer, O. W., "Über die katalytische Isomerisierung einiger Benzin-Kohlenwasserstoffe," Thesis, Eidgenössischen Technischen Hochschule, Zürich, published by Deutsche Druckerie, Prague (1940), 73 pp.
40. Beath, G. B., *J. Soc. Chem. Ind.*, **52**, 338T-340T (1933).
41. Béhal, A., *Ann. chim. phys. (6)*, **15**, 408-432 (1888).
42. —, *Bull. soc. chim. (2)*, **49**, 581-584 (1888).
43. —, *Ibid.*, **50**, 629-631 (1888).
- 43a. Belov, V. N., and Lebedev, B. M., *J. Gen. Chem. (U.S.S.R.)*, **10**, 1543-1546 (1940).
44. Bergmann, E., *Ber.*, **63B**, 1037-1044 (1930).
45. —, *J. Am. Chem. Soc.*, **60**, 1798-1799 (1938).
46. —, *J. Chem. Soc.*, 1938, 1291-1292.
47. —, and Bergmann, F., *J. Am. Chem. Soc.*, **59**, 1443-1450 (1937).
48. —, —, *Ibid.*, **60**, 1805-1807 (1938).
49. —, and Blum-Bergmann, O., *Ibid.*, **58**, 1678-1681 (1936).
50. —, and Bondi, A., *Ber.*, **64B**, 1455-1480 (1931).
51. —, Taubadel, H., and Weiss, H., *Ber.*, **64B**, 1493-1501 (1931).

52. —, and Weiss, H., *Ber.*, **63B**, 1173-1175 (1930).
53. —, —, *Ber.*, **64B**, 1485-1493 (1931).
54. —, —, *Ann.*, **480**, 49-50 (1930).
55. —, —, *Ann.*, **480**, 59-64 (1930).
56. —, and Weizmann, A., *J. Org. Chem.*, **4**, 266-269 (1939).
57. —, Winter, D., and Schreiber, W., *Ann.*, **500**, 122-136 (1933).
- 57a. —, and Zwecker, O., *Ann.*, **487**, 155-163 (1931).
58. Bergmann, F., and Bergmann, E., *J. Am. Chem. Soc.*, **62**, 1699-1704 (1940).
- 58a. Berkman, S., Morrell, J. C., and Egloff, G., "Catalysis," Reinhold Publishing Corp., New York (1940), pp. 629-640, 988-997, 1048, and 1062.
59. Bernthsen, W., *Ann.*, **415**, 274-290 (1918).
60. Berthelot, M. P. E., *Ann. chim. phys. (3)*, **39**, 5-22 (1853).
61. —, *Bull. soc. chim. (2)*, **10**, 341-347 (1868); *Compt. rend.*, **67**, 394-398, 952-954 (1868); *Jahresber. Fortschr. Chem.*, **1868**, 376-377, 411.
62. —, *Compt. rend.*, **129**, 483-491 (1899); *Ann. chim. phys. (7)*, **20**, 27-42 (1900).
63. —, "Les Carbures d'Hydrogène," Gauthier-Villars, Imprimeur-Libraire, Paris (1901), Vol. II, pp. 181-184.
64. Berthoud, A., and Urech, C., *J. chim. phys.*, **27**, 291-306 (1930).
65. Bertram, J., and Walbaum, H., *J. prakt. Chem. (2)*, **49**, 1-15 (1894).
- 65a. Bilham, P., and Kon, G. A. R., *J. Chem. Soc.*, **1940**, 1469-1474.
- 65b. Birch, S. F., and Dunstan, A. E., *Trans. Faraday Soc.*, **35**, 1013-1020 (1939).
- 65c. —, —, Fidler, A. E., Pim, F. B., and Tait, T., *Ind. Eng. Chem.*, **31**, 884-891, 1079-1083 (1939).
66. Blackie, W. J., *J. Soc. Chem. Ind.*, **49**, 26T-27T (1930).
67. Blair, C. M., and Henze, H. R., *J. Am. Chem. Soc.*, **54**, 1538-1545 (1932).
68. Bloch, H. S., Private Communication, Nov. 18, 1938.
- 68a. —, Private Communication, June 30, 1941.
69. Blum-Bergmann, O., *Ber.*, **65B**, 109-122 (1932).
- 69a. Bode, H., *Ber.*, **70B**, 1167-1186 (1937).
70. Böeseken, J., de Groot, M., and W. van Lookeren Campagne C. Jzn., *Rec. trav. chim.*, **37**, 255-265 (1918).
71. —, and Sillevius, K. H. A., *Proc. Acad. Sci. Amsterdam*, **16**, 499-506 (1913) (in English); *Verslag Akad. Wetenschappen*, **22**, 441-449 (1913) (in Dutch).
- 71a. —, Slooff, G., and Lutgerhorst, A. G., *Proc. Acad. Sci. Amsterdam*, **34**, 932-940 (1931).
- 71aa. Bogert, M. T., *Chem. Rev.*, **10**, 265-294 (1932).
- 71b. —, *J. Chem. Ed.*, **11**, 203-207 (1934).
- 71c. —, in H. Gilman's "Organic Chemistry," John Wiley and Sons, Inc., New York (1938), Vol. II, pp. 1138-1219.
72. —, and Davidson, D., *J. Am. Chem. Soc.*, **56**, 185-190 (1934).
73. —, —, and Roblin Jr., R. O., *Ibid.*, **56**, 248 (1934).
74. Bouchardat, G., and Lafont, J., *Ann. chim. phys. (6)*, **9**, 507-534 (1886).
75. —, —, *Ibid.*, **16**, 236-251 (1889).
76. —, —, *Compt. rend.*, **113**, 551-553 (1891).
77. —, —, *Ibid.*, **126**, 755-757 (1898).
78. —, and Oliviero, *Bull. soc. chim. (3)*, **9**, 364-368 (1893).
79. Bouis, M., *Ann. chim. (10)*, **9**, 403-465 (1928).
80. Bourguet, M., *Ibid.*, **3**, 191-235 (1925).
81. —, *Ibid.*, **3**, 325-389 (1925).
82. —, *Ibid.*, **3**, 202-204, 336 (1925).
83. —, *Compt. rend.*, **179**, 686-688 (1924).
- 83a. Bragg, L. B., *Ind. Eng. Chem. (Anal. Ed.)*, **11**, 283-287 (1939).
84. Brand, K., *Ber.*, **54B**, 1987-2006 (1921).
85. —, *Z. Elektrochem.*, **16**, 669-672 (1910).
86. —, and Matsui, M., *Ber.*, **46**, 2942-2951 (1913).
87. Brandt, C. W., *New Zealand J. Sci. Tech.*, **20**, 8B-15B (1938); *Chem. Abs.*, **33**, 551 (1939); *Chem. Zentr.*, **1939**, II, 856-857.
88. Braun, J. von, and Manz, G., *Ber.*, **62B**, 1059-1065 (1929).
- 88a. Bredt, J., in "Festschrift Adolph Wüllner," Verlag von B. G. Teubner, Leipzig (1905), pp. 91-127.
89. —, *Ann.*, **437**, 1-13 (1924).
90. Briggs, L. H., *J. Chem. Soc.*, **1937**, 79-80.
- 90a. —, *Trans. Roy. Soc., New Zealand*, **70**, Part 3, 173-174 (1940); *Chem. Abs.*, **35**, 3995 (1941).
91. British and Continental Camphor Co., Ltd., French Patent 412,668, July 17, 1910; British Patent 10,227, Sept. 22, 1910.
92. Brockway, L. O., and Cross, P. C., *J. Am. Chem. Soc.*, **58**, 2407-2409 (1936).
- 92a. Brooks, D. B., Howard, F. L., and Crafton Jr., H. C., *J. Research Nat'l. Bur. Standards*, **24**, 33-45 (1940) (Research Paper No. 1271).
93. Brunner, H., and Farmer, E. H., *J. Chem. Soc.*, **1937**, 1039-1046.
94. Bruun, J. H., *Ind. Eng. Chem. (Anal. Ed.)*, **8**, 224-226 (1936).
- 94a. —, and West, S. D., *Ibid.*, **9**, 247-248 (1937).
95. Burk, R. E., in National Research Council's "Twelfth Report of the Committee on Catalysis," John Wiley and Sons, Inc., New York (1940), pp. 269-270.
- 95a. Burnop, V. C. E., Elliott, G. H., and Linstead, R. P., *J. Chem. Soc.*, **1940**, 727-735.
- 95b. —, and Linstead, R. P., *J. Chem. Soc.*, **1940**, 720-727.
- 95c. Caesar, P. D., and Francis, A. W., Papers Presented before the Petroleum Division of the American Chemical Society, Atlantic City Meeting, Sept. 8-12, 1941, pp. 253-256; *Ind. Eng. Chem.*, **33**, 1426-1428 (1941).
96. Calingaert, G., and Beatty, H. A., *J. Am. Chem. Soc.*, **58**, 51-54 (1936).
97. —, and Flood, D. T., *Ibid.*, **57**, 956 (1935).
- 97a. Campbell, K. N., and Eby, L. T., *Ibid.*, **63**, 216-219 (1941).
98. Carr, E. P., *Ibid.*, **51**, 3041-3053 (1929).
99. —, and Stücklen, H., *Ibid.*, **59**, 2138-2141 (1937).
100. Carrie, M. S., *J. Soc. Chem. Ind.*, **51**, 367T-368T (1932).
101. Carter, F. D., Copp, F. C., Rao, B. S., Simonsen, J. L., and Subramaniam, K. S., *J. Chem. Soc.*, **1939**, 1504-1509.

102. Carter, G. P., and Gillam, A. E., *Biochem. J.*, **33**, 1325-1331 (1939).
103. Carter, P. G., Smith, H. G., and Read, J., *J. Soc. Chem. Ind.*, **44**, 543T-547T (1925).
104. Chambers, T. S., and Kistiakowsky, G. B., *J. Am. Chem. Soc.*, **56**, 399-405 (1934).
105. Charlton, R. W., and Day, A. R., *Ind. Eng. Chem.*, **29**, 92-95 (1937).
106. Clemo, G. R., Raper, R., and Robson, A. C., *J. Chem. Soc.*, **1939**, 431-435.
107. Clover, A. M., *Am. Chem. J.*, **39**, 613-649 (1908).
108. —, *Philippine J. Sci.*, **2**, 1-40 (1907); *Chem. Zentr.*, **1907**, I, 1793-1795.
109. Coffman, D. D., *J. Am. Chem. Soc.*, **55**, 695-698 (1933).
110. —, Blair, C. M., and Henze, H. R., *Ibid.*, **55**, 252-253 (1933).
111. Cohen Henriquez, P., *Proc. Acad. Sci. Amsterdam*, **37**, 532-547 (1934) (in English).
112. Conant, J. B., and Carlson, G. H., *J. Am. Chem. Soc.*, **51**, 3464-3469 (1929).
113. Cook, J. W., Dansi, A., Hewett, C. L., Iball, J., Mayneord, W. V., and Roe, E., *J. Chem. Soc.*, **1935**, 1319-1325.
114. —, and Haslewood, G. A. D., *Ibid.*, **1935**, 767-770.
115. —, —, and Robinson, A. M., *Ibid.*, **1935**, 667-671.
116. —, and Hewett, C. L., *Ibid.*, **1933**, 1098-1111.
117. —, —, *Ibid.*, **1934**, 365-377.
118. —, —, *Ibid.*, **1936**, 62-71.
119. —, —, Mayneord, W. V., and Roe, E., *Ibid.*, **1934**, 1727-1738.
120. —, —, and Robinson, A. M., *Ibid.*, **1939**, 168-177.
121. —, and Lawrence, C. A., *Ibid.*, **1936**, 1431-1434.
122. —, —, *Ibid.*, **1937**, 817-827.
123. —, and Robinson, A. M., *Ibid.*, **1938**, 505-513.
124. —, —, and Goulden, F., *Ibid.*, **1937**, 393-396.
125. Corson, B. B., and Ipatieff, V. N., *J. Am. Chem. Soc.*, **61**, 1056-1057 (1939).
126. Courtot, C., *Ann. chim. (9)*, **5**, 52-108 (1916).
127. —, *Compt. rend.*, **160**, 523-526 (1915).
128. Cowan, D. M., Jeffrey, G. H., and Vogel, A. I., *Chemistry & Industry*, **17**, (58, No. 23), 559 (1939); *J. Chem. Soc.*, **1939**, 1862-1865.
129. Cox, M. V., *Bull. soc. chim. (4)* **37**, 1549-1553 (1925).
130. Cramer, P. L., and Glasebrook, A. L., *J. Am. Chem. Soc.*, **61**, 230-232 (1939).
131. Daniels, F., "Chemical Kinetics," Cornell University Press, Ithaca, New York, (1938), pp. 239-243.
- 131a. Davidson, D., and Feldman, J., Abstracts of Papers, 100th Meeting of American Chemical Society, Detroit, Mich., Sept. 9-13, 1940, page M-30.
- 131b. Davies, G. F., and Gilbert, E. C., *J. Am. Chem. Soc.*, **63**, 1585-1586 (1941).
132. Davis, D. W., and Marvel, C. S., *Ibid.*, **53**, 3840-3851 (1931).
133. Delépine, M., and Adida, A., *Bull. soc. chim. (4)*, **39**, 782-788 (1926).
- 133a. —, Reisman, J., and Suau, E., *Ibid.*, **47**, 966-986 (1930).
134. Demjanov, N. J., and Dojarenko, M. N., *Ber.*, **55B**, 2718-2727 (1922).
- 134a. Denisenko, Y. I., and Naber, A. D., *J. Gen. Chem. (U. S. S. R.)*, **10**, 193-201 (1940); *Chem. Abs.*, **34**, 7283-7284 (1940).
135. Desgrez, A., *Ann. chim. phys. (7)*, **3**, 209-246 (1894).
- 135a. DeSimo, M., McMillan, F., and Cheney, H., unpublished work of Shell Development Co., mentioned by G. C. A. Schuit, H. Hoog, and J. Verheus, *Rec. trav. chim.*, **59**, 793-810 (1940).
136. Deussen, E., Loesche, A., and Klemm, A., *Ann.*, **369**, 41-56 (1909).
137. —, and Meyer, K., *J. prakt. Chem. (2)*, **90**, 328-329 (1914).
138. Deville, S.-C., *Ann. chim. phys. (2)*, **75**, 37-80 (1840).
139. Dobrianski, A. F., and Saprikin, F. Y., *J. Gen. Chem. (U. S. S. R.)*, **9**, 1313-1314 (1939); *Oil Gas J.*, **39**, No. 13, 48 (1940).
140. Dojarenko, M. N., *Ber.*, **59B**, 2933-2948 (1926); *J. Russ. Phys.-Chem. Soc.*, **58**, 1-15 (1926).
- 140a. Dolliver, M. A., Gresham, T. L., Kistiakowsky, G. B., and Vaughan, W. E., *J. Am. Chem. Soc.*, **59**, 831-841 (1937).
141. Drake, N. L., and McVey, W. C., *J. Org. Chem.*, **4**, 464-471 (1939).
- 141a. Dubosc, A., and Luttringer, A., "Rubber," C. Griffin and Co., Ltd., London (1918), p. 253.
142. Dufraisse, C., *Bull. soc. chim. (5)*, **3**, 1847-1857 (1936).
143. —, Masumoto, B., and Buret, R., *Bull. soc. chim. (4)*, **51**, 74-80 (1932).
144. Dupont, G., and Dulou, R., *Compt. rend.*, **201**, 219-221 (1935).
145. —, —, *Ibid.*, **202**, 1861-1863 (1936).
146. —, —, *Atti X° cong. intern. chim.*, **3**, 123-129, 129-139 (1939) (in French); *Chem. Abs.*, **33**, 9312-9313 (1939); *Angew. Chem.*, **51**, 755-756 (1938) (erroneous abstract).
147. —, —, and Desreux, V., *Bull. soc. chim. (5)*, **6**, 83-91 (1939).
148. —, —, and Picoux, R., *Ibid.*, **5**, 322-336 (1938).
149. —, and Gachard, R., *Bull. soc. chim. (4)*, **51**, 1579-1594 (1932).
150. Durland, J. R., and Adkins, H., *J. Am. Chem. Soc.*, **60**, 1501-1505 (1938).
- 150a. Eck, J. C., and Hollingsworth, E. W., *Ibid.*, **63**, 107-111 (1941).
151. Egloff, G., "Physical Constants of Hydrocarbons," Reinhold Publishing Corp., New York (1939-); Vol. I: Paraffins, Olefins, Acetylenes and Other Aliphatic Hydrocarbons, (1939), 403 pp.; Vol. II: Cyclanes, Cycloenes, Cyclynes, and Other Alicyclic Hydrocarbons, (1940), 605 pp.; 3 other volumes in preparation (American Chemical Society Monograph Series No. 78).
152. —, *Ibid.*, Vol. I, pp. 49-59.
153. —, *Ibid.*, Vol. I, pp. 169-171.
154. —, *Ibid.*, Vol. I, pp. 176-178.
155. —, "The Reactions of Pure Hydrocarbons," Reinhold Publishing Corp., New York (1937), 897 pp. (American Chemical Society Monograph Series No. 73).
156. —, *Ibid.*, pp. 459-460.
157. —, *Ibid.*, pp. 710-711.
158. —, Morrell, J. C., Thomas, C. L., and Bloch, H. S., Paper presented at Baltimore, Md. Meeting of American Chemical Society, April 3-7, 1939; *J. Am. Chem. Soc.*, **61**, 3571-3580 (1939).
159. —, and Parrish, C. I., *Chem. Rev.*, **19**, 145-161 (1936).
- 159a. —, and Van Arsdell, P. M., *J. Inst. Petroleum*, **27**, 121-142 (1941).
160. —, Wilson, E., Hulla, G., and Van Arsdell, P. M., *Chem. Rev.*, **20**, 345-411 (1937).
161. Egorova, V., *J. Russ. Phys.-Chem. Soc.*, **43**, 1116-1124 (1911).
162. Eijkman, J. F., *Chem. Weekblad*, **1**, 7-12 (1903); *Chem. Zentr.*, **1903**, II, 989.

- 162a. Eisenlohr, F., *Z. physik. Chem.*, **75**, 585-607 (1911).
163. Eltekov, A., *J. Russ. Phys.-Chem. Soc.*, **14**, 355-396 (1882).
164. —, and Lagermark, H., *Ber.*, **12**, 854 (1879).
165. Enderlin, L., *Compt. rend.*, **193**, 1432-1434 (1931).
- 165a. Engel, W. F., (assignor to Shell Development Co.), U. S. Patent 2,208,362, July 16, 1940.
166. Engler, C., and Rogowski, W., in C. Engler's "Die Neueren Ansichten über die Entstehung des Erdöles," Verlag für Fachliteratur G.m.b.H., Berlin (1907), pp. 23-24.
167. Enklaar, C. J., *Rev. trav. chim.*, **26**, 157-179 (1907).
168. —, *Ibid.*, **27**, 422-434 (1908).
169. —, *Ibid.*, **36**, 215-246 (1917).
170. Errington, K. D., and Linstead, R. P., *J. Chem. Soc.*, **1938**, 666-672.
171. Ertchikovski, G., *J. Russ. Phys.-Chem. Soc.*, **28**, 132 (1896); *Bull. soc. chim. (3)*, **16**, 1584-1586 (1896).
172. Ewell, R. H., *Ind. Eng. Chem.*, **31**, 267-273 (1939).
- 172a. —, and Hardy, P. E., in Papers Presented before the Petroleum Division of the American Chemical Society, Atlantic City Meeting, Sept. 8-12, 1941, pp. 231-241.
173. Eyring, H., *Chem. Rev.*, **17**, 65-77 (1935).
174. —, *J. Chem. Phys.*, **3**, 107-115 (1935).
175. Farley, E. D., and Marvel, C. S., *J. Am. Chem. Soc.*, **58**, 29-34 (1936).
176. Faworsky, A., *J. prakt. Chem. (2)*, **37**, 382-395 (1888).
177. —, *Ibid.*, **37**, 417-431 (1888); *J. Russ. Phys.-Chem. Soc.*, **19**, 553-566 (1887); *Ber.*, **21**, Ref., 177 (1888).
178. —, *J. prakt. Chem. (2)*, **37**, 531-536 (1888).
179. —, *Ibid.*, **44**, 208-238 (1891).
180. —, *J. Russ. Phys.-Chem. Soc.*, **19**, (1), 414-428 (1887); *Ber.*, **20**, Ref., 781-783 (1887).
181. —, and Borgmann, I., *Ber.*, **40**, 4863-4875 (1907).
182. —, Sakara, N., Shibaev, A., Opel, E., and Korolev, S., *J. Russ. Phys.-Chem. Soc.*, **50**, 43-80 (1918).
183. Fichter, F., and Alber, E., *J. prakt. Chem. (2)*, **74**, 332-339 (1906).
184. —, and Hirsch, S., *Ber.*, **34**, 2188-2191 (1901).
- 184a. Fieser, L. F., in H. Gilman's "Organic Chemistry," John Wiley and Sons, Inc., New York (1938), p. 94.
185. —, and Hershberg, E. B., *J. Am. Chem. Soc.*, **60**, 1658-1665 (1938).
186. —, Joshel, L. M., and Seligman, A. M., *Ibid.*, **61**, 2134-2139 (1939).
187. Filipov, O., "Bau der Kohlenwasserstoffe von G. G. Gustavson, gewonnen aus Pentaerythrit" (1914), p. 68; cf. M. Dojarenko, *Ber.*, **59B**, 2933-2948 (1926).
188. —, *J. prakt. Chem. (2)*, **93**, 162-182 (1916).
189. —, *J. Russ. Phys.-Chem. Soc.*, **46**, 1141-1199 (1914).
190. Fittig, R., and Batt, L., *Ann.*, **331**, 160-172 (1904).
191. Flavitsky, F., *Ber.*, **12**, 1022 (1879).
192. Ford, J. H., Thompson, C. D., and Marvel, C. S., *J. Am. Chem. Soc.*, **57**, 2619-2623 (1935).
193. Frey, F. E., *Oil Gas J.*, **35**, No. 34, pp. 40, 43, 46, 49 (1937).
194. —, and Hepp, H. J., *Ind. Eng. Chem.*, **28**, 1439-1445 (1936).
195. Friedel, C., and Crafts, J. M., *Bull. soc. chim. (2)*, **39**, 195 (1883).
196. —, —, *Compt. rend.*, **100**, 692-698 (1885).
197. Friedmann, W., *Ber.*, **49**, 1344-1352 (1916); *Brennstoff-Chem.*, **8**, 257-259 (1927); *Oil Gas J.*, **29**, No. 31, pp. 32, 106-107 (1930); **37**, No. 45, 88 (1939).
198. Frost, A. V., *J. Gen. Chem. (U. S. S. R.)*, **9**, 1813-1818 (1939); *Refiner Natural Gasoline Mfr.*, **20**, No. 1, 66-69 (1941).
- 198a. —, Transactions of the December, 1936, Organic Chemistry Session of the Academy of Sciences of U. S. S. R., publ. by the Academy of Sciences U. S. S. R., Moscow-Leningrad, 1939, 99-112; Translation S-108 of J. G. Tolpin.
199. —, Rudkovsky, D. M., and Serebriakova, E. K., *Compt. rend. acad. sci. U. R. S. S.*, **4**, 373-376 (1936) (in English).
200. —, Serebriakova, E. K., and Rudkovsky, D. M., Russian Patent 51,181, June 30, 1937; *Chem. Abs.*, **33**, 4599 (1939).
201. Fujita, Y., *J. Chem. Soc. Japan*, **53**, 847-852 (1932).
202. —, *Ibid.*, **55**, 1-5 (1934).
203. Fussteig, R., *Refiner Natural Gasoline Mfr.*, **17**, 168-171 (1938).
204. Gadzjacki, V. T., *Jahresber. Fortschr. Chem.*, **1889**, 707; *J. Russ. Phys.-Chem. Soc.*, **20**, (1), 706 (1888).
- 204a. Gallas, G., and Montañés, J. M., *Anales soc. espan. fís. quim.*, **28**, 1163-1213 (1930); *Chem. Abs.*, **25**, 506-507 (1931).
205. Ganapathi, K., *J. Indian Inst. Sci.*, **22A**, (new series 2, No. 2), 155-169 (1939); *Brit. Chem. Abs.-A*, **II**, 1939, 516.
206. Gaponenkov, T. K., *J. Gen. Chem. (U. S. S. R.)*, **4**, 1128-1129 (1934).
- 206a. Gascoigne, R. M., *J. Proc. Roy. Soc. N. S. Wales*, **74**, 353-358 (1941); *Chem. Abs.*, **35**, 2877-2878 (1941).
- 206b. —, *Ibid.*, **74**, 359-364 (1941); *Chem. Abs.*, **35**, 2876 (1941).
207. Gaverdovskaya-Yuschkevitsch, M. V., *Sci. Repts. Moscow State Univ.* 1936, No. 6, 263-266; *Chem. Abs.*, **32**, 2524 (1938).
208. Genvresse, P., *Ann. chim. phys. (7)*, **26**, 31-39 (1902).
209. —, *Compt. rend.*, **134**, 360-362 (1902).
210. Gillam, A. E., and El Ridi, M. S., *Nature*, **136**, 914-915 (1935); *Biochem. J.*, **30**, 1735-1742 (1936).
211. —, —, and Kon, S. K., *Biochem. J.*, **31**, 1605-1610 (1937).
212. Gillet, A., *Bull. soc. chim. Belg.*, **29**, 192-199 (1920).
213. Gilman, H., "Organic Chemistry," John Wiley and Sons, Inc., New York, 1938, Vol. I, pp. 394-395.
214. Ginzburg, Y. I., *J. Gen. Chem. (U. S. S. R.)*, **8**, 1029-1041 (1938).
215. Glasebrook, A. L., and Lovell, W. G., *J. Am. Chem. Soc.*, **61**, 1717-1720 (1939).
216. —, Phillips, N. E., and Lovell, W. G., *Ibid.*, **58**, 1944-1948 (1936).
- 216a. Glasstone, S., Laidler, K. J., and Eyring, H., "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, 1941, pp. 10-27, 183-193, 323-333.

217. Goebel, M. T., and Marvel, C. S., *J. Am. Chem. Soc.*, **55**, 3712-3715 (1933).
- 217a. Goldblatt, L. A., and Palkin, S., Abstracts of Papers Presented before Division of Organic Chemistry of the American Chemical Society, St. Louis Meeting, April 7-11, 1941, pp. M-18 to M-19 (Paper I).
- 217b. —, —, *Ibid.*, pp. M-19 to M-20 (Paper II).
218. Goldwasser, S., and Taylor, H. S., *J. Am. Chem. Soc.*, **61**, 1260-1263 (1939).
219. —, —, *Ibid.*, **61**, 1751-1761 (1939).
220. —, —, *Ibid.*, **61**, 1762-1765 (1939).
221. —, —, *Ibid.*, **61**, 1766-1769 (1939).
222. Gomberg, M., *Ber.*, **36**, 376-388 (1903).
223. —, *Ber.*, **40**, 1847-1888 (1907).
224. Gould, D. W., in "Science of Petroleum," edited by A. E. Dunstan, A. W. Nash, B. T. Brooks, and H. Tizard, Oxford University Press, London, 1938, Vol. II, pp. 1241-1242.
225. Graebe, C., *Ber.*, **27**, 952-955 (1894).
226. Grignard, V., *Ann. chim. phys.* (7), **24**, 433-490 (1901).
227. —, *Bull. soc. chim.* (3), **21**, 576-578 (1899).
228. —, and Stratford, R., *Compt. rend.*, **178**, 2149-2152 (1924); *Bull. soc. chim.* (4), **35**, 931-932 (1924).
229. —, and Tcheoufaki, *Rec. trav. chim.*, **48**, 899-903 (1929); *Compt. rend.*, **188**, 1531-1534 (1929).
230. Grinberg, R., Thesis, Grenoble (1914); cf. C. Courtot, *Ann. chim.* (9), **5**, 106-107 (1916).
231. Griner, G., *Ann. chim. phys.* (6), **26**, 305-394 (1892).
232. Grosse, A. V., and Mavity, J. W., unpublished work. Mentioned by G. Egloff, V. I. Komarewsky, and G. Hulla in Papers Presented before the Petroleum Division of the American Chemical Society, Part I, Baltimore Meeting, April 3-7, 1939, page J-1.
- 232a. —, and Pines, H., (assignors to Universal Oil Products Co.), U. S. Patent 2,225,776, Dec. 24, 1940.
233. Groth, P., *Z. Kryst. Mineral.*, **5**, 476-482 (1881).
234. Guest, H. H., *J. Am. Chem. Soc.*, **50**, 1744-1746 (1928).
235. Gurvitch, L. G., *J. Russ. Phys.-Chem. Soc.*, **47**, 827-830 (1915); *J. Chem. Soc.*, **108**, Part 1, 933-934 (1915).
236. —, *Z. physik. Chem.*, **107**, 235-248 (1923).
237. Gustavson, G., *J. prakt. Chem.* (2), **54**, 97-104 (1896).
238. —, Letter to N. J. Demjanov, dated Oct. 30, 1901; cf. M. Dojarenko, *Ber.*, **59B**, 2933-2948 (1926).
239. —, and Demjanov, N. J., *J. prakt. Chem.* (2), **38**, 201-207 (1888).
240. Halley, L. F., and Marvel, C. S., *J. Am. Chem. Soc.*, **54**, 4450-4454 (1932).
241. Harkness, R. W., *Ibid.*, **58**, 1058-1059 (1936).
242. Harmon, J., and Marvel, C. S., *Ibid.*, **55**, 1716-1722 (1933).
243. Harries, C., *Ber.*, **35**, 3256-3266 (1902).
244. Heilbron, I. M., Kamm, E. D., and Owens, W. M., *J. Chem. Soc.*, **1926**, 1630-1644.
245. Heise, R., and Töhl, A., *Ann.*, **270**, 155-171 (1892).
246. Henderson, G. G., and Robertson, A., *J. Chem. Soc.*, **125**, 1992-1996 (1924).
247. Henze, H. R., and Blair, C. M., *J. Am. Chem. Soc.*, **53**, 3077-3085 (1931).
248. —, —, *Ibid.*, **55**, 680-686 (1933).
249. —, —, *Ibid.*, **56**, 157 (1934).
250. Hewett, C. L., *J. Chem. Soc.*, **1938**, 193-196.
251. Hibben, J. H., "The Raman Effect and Its Chemical Applications," Reinhold Publishing Corp., New York, 1939, (American Chemical Society Monograph Series No. 80).
252. Hibbit, D. C., and Linstead, R. P., *J. Chem. Soc.*, **1936**, 470-476.
253. —, —, and Millidge, A. F., *Ibid.*, **1936**, 476-478.
254. Hirao, N., and Takano, T., *J. Chem. Soc. Japan*, **58**, 213-221 (1937).
255. —, —, *Ibid.*, **59**, 95-101 (1938).
256. —, —, *Ibid.*, **59**, 193-198 (1938).
257. Hoog, H., (assignor to Shell Development Co.), Canadian Patent 388,423, April 30, 1940; *Chem. Abs.*, **34**, 4839 (1940).
- 257a. —, (assignor to Shell Development Co.), U. S. Patent 2,217,252, Oct. 8, 1940.
- 257b. Houben, J., "Die Methoden der organischen Chemie," George Thieme, Leipzig, 1923, Vol. III, p. 823.
- 257c. Hückel, W., Neunhoeffer, O., Gercke, A., and Frank, E., *Ann.*, **477**, 99-160 (1930).
258. —, and Tappe, W., *Ann.*, **537**, 113-131 (1939).
- 258a. —, —, and Legutke, G., *Ann.*, **543**, 191-230 (1940).
259. Hugel, G., and Szayna, A., *Ann. combustibles liquides*, **1**, 781-836 (1926).
260. Hunter, W. H., and Yohe, R. V., *J. Am. Chem. Soc.*, **55**, 1248-1252 (1933).
261. Hurd, C. D., *Ind. Eng. Chem.*, **26**, 50-55 (1934).
262. —, and Bollman, H. T., *J. Am. Chem. Soc.*, **55**, 699-702 (1933).
263. —, and Christ, R. E., *Ibid.*, **59**, 2161-2165 (1937).
264. —, and Goldsby, A. R., *Ibid.*, **56**, 1812-1815 (1934).
265. —, Goodyear, G. H., and Goldsby, A. R., *Ibid.*, **58**, 235-237 (1936).
266. I. G. Farbenindustrie A.-G. (F. Runge and M. Mueller-Cunradi, inventors), German Patent 583,790, Sept. 13, 1933.
267. —, (F. Runge and M. Mueller-Cunradi, inventors), U. S. Patent 1,914,674, June 20, 1933.
268. Imoto, M., *J. Soc. Chem. Ind. Japan (Supplement)*, **41**, 209B-212B (1938).
269. —, *Ibid.*, **42**, 183B-186B (1939).
270. Ipatieff, V. N., *Ber.*, **35**, 1057-1064 (1902).
271. —, *Ber.*, **36**, 2003-2013 (1903); *J. Russ. Phys.-Chem. Soc.*, **35**, 577 (1903).
272. —, *Ber.*, **43**, 3546-3553 (1910).
273. —, "Catalytic Reactions at High Pressures and Temperatures," The Macmillan Co., New York, 1936, p. 154.
274. —, *Ibid.*, p. 556.
275. —, and Dowgelewitsch, N., *Ber.*, **44**, 2987-2992 (1911); *J. Russ. Phys.-Chem. Soc.*, **43**, 1431-1436 (1911).
- 275a. —, and Dvorkovitz, V., Abstracts of Papers Presented before Division of Organic Chemistry of the American Chemical Society, Atlantic City Meeting, Sept. 8-12, 1941, page M-28.
276. —, and Grosse, A. V., *Ind. Eng. Chem.*, **28**, 461-464 (1936).

277. —, —, *J. Am. Chem. Soc.*, **57**, 1616-1621 (1935).
278. —, —, Pines, H., and Komarewsky, V. I., *Ibid.*, **58**, 913-915 (1936).
279. —, and Huhn, W., *Ber.*, **36**, 2014-2016 (1903); *J. Russ. Phys.-Chem. Soc.*, **35**, 603-605 (1903).
280. —, and Komarewsky, V. I., *J. Am. Chem. Soc.*, **56**, 1926-1928 (1934).
281. —, —, and Grosse, A. V., *Ibid.*, **57**, 1722-1724 (1935).
282. —, Orlov, N., and Petrov, A., "Aluminiumoxyd als Katalysator in der organischen Chemie," Akademische Verlagsgesellschaft, m.b.H., Leipzig, 1929, 91 pp.
283. —, and Pines, H., Papers Presented before the Petroleum Division of the American Chemical Society, Dallas Meeting, April 19, 1938, pp. 85-91.
284. —, —, (assignors to Universal Oil Products Co.), U. S. Patent 2,169,494, Aug. 15, 1939.
285. —, —, and Schaad, R. E., *J. Am. Chem. Soc.*, **56**, 2696-2698 (1934).
286. —, —, and Schmerling, L., *Ibid.*, **60**, 353-354 (1938).
287. —, —, —, *J. Org. Chem.*, **5**, 253-263 (1940).
288. —, and Sdzitowiecky, W., *Ber.*, **40**, 1827-1830 (1907); *J. Russ. Phys.-Chem.*, **38**, 1178-1180 (1906).
289. —, and Tichotsky, N., *J. Russ. Phys.-Chem. Soc.*, **36**, 760-762 (1904); cf. V. N. Ipatieff, "Catalytic Reactions at High Pressures and Temperatures," The Macmillan Co., New York, 1936, pp. 158-159.
290. Jacobsen, O., *Ber.*, **18**, 338-344 (1885).
291. Jones, R. L., and Linstead, R. P., *J. Chem. Soc.*, 1936, 616-621.
292. Jozitsch, J., *J. Russ. Phys.-Chem. Soc.*, **29**, 90-97 (1897); *Chem. Zentr.*, **1897**, I, 1011-1012.
293. Kadzhinov, V. N., *Ukrain. Chem. J.*, **8**, 333-346 (1933); *Chem. Abs.*, **29**, 2161 (1935).
294. Kafuku, K., and Nozoe, T., *Bull. Chem. Soc. Japan*, **6**, 111-118 (1931) (in English).
295. Karrer, P., Helfenstein, A., Wehrli, S., and Wettstein, A., *Helv. Chim. Acta*, **13**, 1084-1099 (1930).
296. —, and Solmssen, U., *Ibid.*, **20**, 682-690 (1937).
297. —, —, and Gugelmann, W., *Ibid.*, **20**, 1020-1024 (1937).
- 297a. Karzhev, V. I., Sever'yanova, M. G., and Sivova, A. N., *J. Applied Chem. (U. S. S. R.)*, **9**, 269-277 (in English, 278) (1936); *Khim. Tverdogo Topliva*, **7**, 282-298 (1936).
298. Kassel, L. S., *J. Chem. Phys.*, **4**, 276-282 (1936).
299. Kay, F. W., and Morton, A., *J. Chem. Soc.*, **105**, 1565-1583 (1914).
300. Kelber, C., and Schwarz, A., *Ber.*, **45**, 1946-1952 (1912).
301. Kharasch, M. S., Private Communication to M. L. Sherrill, B. Otto, and L. W. Pickett, *J. Am. Chem. Soc.*, **51**, 3023-3033 (1929).
302. —, and Darkis, F. R., *Chem. Rev.*, **5**, 571-602 (1928).
303. —, Mansfield, J. V., and Mayo, F. R., *J. Am. Chem. Soc.*, **59**, 1155 (1937).
- 303a. Kimball, G. E., in National Research Council's "Twelfth Report of the Committee on Catalysis," John Wiley and Sons, Inc., New York, 1940, pp. 1-17.
- 303b. Kimura, S., *J. Chem. Soc. Japan*, **51**, 527-533 (1930); *Mem. Coll. Sci., Kyoto Imp. Univ. (A)*, **14**, 186-193 (1931).
304. Kishner, N., *J. Russ. Phys.-Chem. Soc.*, **43**, 1398-1402 (1911); *Chem. Zentr.*, **1912**, I, 1622-1623.
- 304a. Kistiakowsky, G. B., Ruhoff, J. R., Smith, H. A., and Vaughan, W. E., *J. Am. Chem. Soc.*, **57**, 876-882 (1935).
305. —, —, —, —, *Ibid.*, **58**, 137-145 (1936).
306. —, and Smith, W. R., *Ibid.*, **56**, 638-642 (1934).
307. —, —, *Ibid.*, **58**, 766-768 (1936).
308. Klages, A., *Ber.*, **37**, 2301-2317 (1904).
309. —, *Ber.*, **39**, 2587-2595 (1906).
310. —, *Ber.*, **40**, 2360-2373 (1907).
311. —, and Sommer, F., *Ber.*, **39**, 2306-2315 (1906).
312. Knowlton, J. W., and Rossini, F. D., *J. Research Nat'l. Bur. Standards*, **22**, 415-424 (1939) (Research Paper No. 1193).
313. Koelsch, C. F., *J. Am. Chem. Soc.*, **55**, 3394-3399 (1933).
314. —, *Ibid.*, **56**, 480-484 (1934).
315. —, *Ibid.*, **56**, 1337-1339 (1934).
316. —, and Rosenwald, R. H., *Ibid.*, **59**, 2170-2171 (1937).
- 316a. —, and White, R. V., *J. Org. Chem.*, **6**, 602-611 (1941).
317. Kohler, E. P., *Am. Chem. J.*, **40**, 217-233 (1908).
- 317a. Kohlrausch, K. W. F., and Köppl, F., *Z. physik. Chem.*, **B26**, 209-237 (1934).
318. Komarewsky, V. I., Unpublished work.
319. —, and Riesz, C. H., *J. Am. Chem. Soc.*, **61**, 2524-2525 (1939).
- 319a. Komppa, G., and Beckmann, S., *Ann.*, **522**, 137-150 (1936).
320. —, and Nyman, G. A., *Ann.*, **535**, 252-266 (1938).
- 320a. —, —, *Ann.*, **543**, 111-118 (1940).
321. Kon, G. A. R., and Narracott, E. S., *J. Chem. Soc.*, 1938, 672-676.
322. Kondakov, S.-L., *Parfumerie moderne*, **19**, 212-223 (1926).
323. Krafft, F., and Reuter, L., *Ber.*, **25**, 2243-2251 (1892).
- 323a. Kronstein, A., *Ber.*, **54B**, 1-16 (1921).
324. Kuhn, R., *Inst. intern. chim. Solvay, Conseil chim., 4th Conseil, Brussels, 1931*, p. 364; cf. T. W. J. Taylor and A. R. Murray, *J. Chem. Soc.*, 1938, 2078-2086; see also K. Freudenberg, "Stereochemie," Franz Deuticke Verlag, Leipzig, 1933, p. 917.
325. Kutscherov, L. M., *J. Russ. Phys.-Chem. Soc.*, **45**, 1634-1654 (1913); *Chem. Zentr.*, **1914**, I, 753-754.
326. —, *Ibid.*, **45**, 1634-1654 (1913); *J. Chem. Soc.*, **104**, Part 1, 1294 (1913).
327. Kuwata, T., *J. Soc. Chem. Ind. Japan (Supplement)*, **32**, 372B-373B (1929).
- 327a. —, *Ibid.*, **39**, 392B-394B (1936).
328. Lafont, J., *Ann. chim. phys. (6)*, **15**, 145-223 (1888).
329. Laughlin, K. C., Nash, C. W., and Whitmore, F. C., *J. Am. Chem. Soc.*, **56**, 1395-1396 (1934).
330. Lebedev, S. V., *J. Russ. Phys.-Chem. Soc.*, **43**, 820-834 (1911); *Chem. Abs.*, **6**, 478-479 (1912); *Chem. Zentr.*, **1911**, II, 1915-1916.
331. —, *J. Russ. Phys.-Chem. Soc.*, **45**, 1372-1373 (1913); *Chem. Abs.*, **9**, 799 (1915); *Chem. Zentr.*, **1914**, I, 1402-1412.
332. —, Andreevski, J., and Matuschkina, A., *Ber.*, **56B**, 2349-2353 (1923).
333. —, and Slobodin, Y. M., *J. Gen. Chem. (U. S. S. R.)*, **4**, 23-30 (1934).
334. Lepin, A. I., *J. Russ. Phys.-Chem. Soc.*, **44**, 1190-1196 (1912).
335. —, and Reich, V. N., *Ibid.*, **47**, 149-160 (1915).

336. Lespicau, R., *Ann. chim. (9)*, 2, 280-292 (1914).
- 336a. Levina, R. Y., *Sci. Reports Moscow State Univ.*, 3, 187-192 (1934); *Chem. Abs.*, 30, 8190 (1936).
337. —, *J. Gen. Chem. (U. S. S. R.)*, 6, 1092-1095 (1936).
338. —, *Ibid.*, 7, 1587-1593 (1937).
339. —, *Ibid.*, 9, 2287-2290 (1939).
340. —, and Chernyak, M. I., *Ibid.*, 7, 402-404 (1937).
341. —, Golub, G. B., and Smirnov, K. M., *Ibid.*, 9, 825-828 (1939).
342. —, and Ivanov, A. I., *Ibid.*, 7, 1866-1867 (1937); *Chem. Abs.*, 32, 507 (1938); *Brit. Chem. Abs.*, A, II, 1938, 47.
- 342a. —, Karelava, L. E., and Elyashberg, I. A., *J. Gen. Chem. (U. S. S. R.)*, 10, 913-916 (1940).
343. —, and Kiryushov, P. Y., *Ibid.*, 9, 1834-1840 (1939).
344. —, and Levina, S. Y., *Ibid.*, 8, 1776-1779 (1938).
- 344a. —, and Panov, E. M., *Ibid.*, 11, 533-536 (1941).
345. —, and Petrov, D. A., *Ibid.*, 7, 747-749 (1937).
346. —, and Potapova, A. A., *Ibid.*, 7, 353-356 (1937).
- 346a. —, and Shcheglova, N. A., *Ibid.*, 11, 527-532 (1941).
347. —, and Trakhtenberg, D. M., *Ibid.*, 6, 764-773 (1936).
348. —, and Tzurikov, F. F., *Ibid.*, 4, 1250-1257 (1934).
349. —, Yuriev, Y. K., and Loschkomoinikov, A. I., *Ibid.*, 7, 341-349 (1937).
- 349a. Levshuk, M. Y., Lyubomilov, V. I., Pesin, L. M., Plotnikova, A. F., and Rutovski, B. N., *J. Applied Chem. (U. S. S. R.)*, 13, 1178-1181 (1940).
350. Lewis, G. N., "Valence and the Structure of Atoms and Molecules," The Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), New York, 1923, p. 113 (American Chemical Society Monograph Series No. 14).
- 350a. —, Magel, T. T., and Lipkin, D., *J. Am. Chem. Soc.*, 62, 2973-2980 (1940).
- 350b. Linstead, R. P., Michaelis, K. O. A., and Thomas, S. L. S., *J. Chem. Soc.*, 1940, 1139-1147.
- 350c. —, Millidge, A. F., Thomas, S. L. S., and Walpole, A. L., *Ibid.*, 1937, 1146-1157.
351. —, —, and Walpole, A. L., *Ibid.*, 1937, 1140-1145.
352. —, and Walpole, A. L., *Ibid.*, 1939, 842-850.
353. —, Wang, A. B., Williams, J. H., and Errington, K. D., *Ibid.*, 1937, 1136-1140.
- 353a. Lipp, M., *Ber.*, 74B, 1-6 (1941).
- 353b. —, *Ber.*, 74B, 6-12 (1941).
354. Lipp, P., *Ann.*, 382, 265-305 (1911).
355. —, *Ber.*, 53B, 769-781 (1920).
- 355a. —, *Ann.*, 480, 298-307 (1930).
- 355b. —, *Ber.*, 68B, 1029-1031 (1935).
- 355c. Lorentz, H. A., *Ann. Physik (3)*, 9, 641-665 (1880).
- 355d. Lorenz, L., *Ann. Physik (3)*, 11, 70-103 (1880).
356. Lucas, H. J., and Moyse, H. W., *J. Am. Chem. Soc.*, 47, 1459-1461 (1925).
357. —, Simpson, T. P., and Carter, J. M., *Ibid.*, 47, 1462-1469 (1925).
- 357a. Lynch, C. S., and Wood, III, J. E., (assignors to Standard Oil Development Co.), U. S. Patent 2,223,180, Nov. 26, 1940.
358. Maitland, P., and Mills, W. H., *J. Chem. Soc.*, 1936, 987-998.
- 358a. Marder, M., *Oel, Kohle, Erdoel, Teer*, 11, 1-5, 41-43, 75-77, 150-152, 182-185, 222-225 (1935).
- 358b. Marvel, C. S., and Himel, C. M., *J. Am. Chem. Soc.*, 62, 1550-1553 (1940).
- 358c. —, Kaplan, J. F., and Himel, C. M., *Ibid.*, 63, 1892-1896 (1941).
359. —, Mueller, M. B., Himel, C. M., and Kaplan, J. F., *Ibid.*, 61, 2771-2775 (1939).
360. —, and Peppel, W. J., *Ibid.*, 61, 895-897 (1939).
361. —, Rieger, W. H., and Mueller, M. B., *Ibid.*, 61, 2769-2771 (1939).
362. Matignon, C., Moureu, H., and Dode, M., *Bull. soc. chim. (5)*, 2, 1169-1181 (1935).
363. Matsuno, K., and Han, K., *Bull. Chem. Soc. Japan*, 10, 220-231 (1935) (in English).
364. —, —, *Ibid.*, 11, 576-586 (1936) (in English).
365. Mayer, F., and Schiffner, R., *Ber.*, 67B, 67-69 (1934).
366. McAteer, J. H., Paper presented at Gibson Island, Maryland, Meeting of Am. Assoc. Adv. Science, June 17-21, 1940.
367. McDowall, F. H., and Finlay, H. J., *J. Soc. Chem. Ind.*, 44, 42T (1925).
368. McKee, R. H., and Szayna, A., *Ind. Eng. Chem.*, 22, 953-956 (1930).
369. Meerwein, H., and van Emster, K., *Ber.*, 53B, 1815-1829 (1920).
370. —, —, *Ber.*, 55B, 2500-2528 (1922).
- 370a. Meinert, R. N., and Hurd, C. D., *J. Am. Chem. Soc.*, 52, 4540-4549 (1930).
371. Mereshkovski, B. K., *J. Russ. Phys.-Chem. Soc.*, 45, 1940-1974 (1913).
372. —, *Ibid.*, 45, 2071-2072 (1913).
373. —, *Ibid.*, 46, 97-123 (1914).
374. Meshcheryakov, A. P., and Kaplan, E. P., *Bull. acad. sci. U. R. S. S., Classe sci. math. nat., Sér. chim.*, 1938, 1055-1060; *Foreign Petroleum Tech.*, 7, No. 11-12, 575-583 (1939).
375. Messerly, G. H., Aston, J. G., and Kennedy, R. M., *J. Am. Chem. Soc.*, 62, 1630-1631 (1940).
- 375a. Meyer, V., and Müller, F., *J. prakt. Chem. (2)*, 46, 161-188 (1892).
376. Mikchailenko, Y. Y., and Krechkov, A. P., *J. Gen. Chem. (U. S. S. R.)*, 6, 102-106 (1936).
377. Mochida, T., *J. Pharm. Soc. Japan*, 53, 936-947 (1933).
378. Mohr, E., *J. prakt. Chem. (2)*, 98, 315-353 (1918); 103, 316-328 (1922).
379. Moldavsky, B. L., Kobilskaya, M. V., and Livschitz, S. E., *J. Gen. Chem. (U. S. S. R.)*, 5, 1791-1797 (1935).
380. —, —, —, *Ibid.*, 6, 616-620 (1936).
- 380a. —, and Livschitz, S. E., *Ibid.*, 4, 948-950 (1934).
381. —, —, *Ibid.*, 5, 422-431 (1935); *Compt. rend. acad. sci. U. R. S. S.*, 1, 507-513 (1935) (in Russian and German).
382. —, and Nisovkina, T. V., *Compt. rend. acad. sci. U. R. S. S.*, 23, 919-920 (1939) (in English); *J. Gen. Chem. (U. S. S. R.)*, 9, 1652-1660 (1939); *Natl. Petroleum News*, 32, No. 48, R-422 to R-428 (1940).
- 382a. —, —, and Shtern, R. A., *J. Gen. Chem. (U. S. S. R.)*, 10, 1183-1188 (1940).
383. Montaland, L., U. S. Patent 999,667, Aug. 1, 1911.
384. Montgomery, C. W., McAteer, J. H., and Franke, N. W., *J. Am. Chem. Soc.*, 59, 1768-1769 (1937).

385. —, —, —, Papers Presented before the Petroleum Division of the American Chemical Society, Part I, Baltimore Meeting, April 3-7, 1939, pp. M-1 to M-12.
386. Moore, G. E., and Parks, G. S., *J. Am. Chem. Soc.*, **61**, 2561-2562 (1939).
387. Moureu, C., Dufraisse, C., and Berchet, G., *Compt. rend.*, **185**, 1085-1087 (1927).
388. —, —, and Enderlin, L., *Ibid.*, **188**, 673-675 (1929).
389. —, —, and Houghton, A. S., *Bull. soc. chim.* (4), **41**, 56-58 (1927).
390. Mulcey, P. A., *Bull. inst. pin*, 1931, 177-181.
391. —, *Ibid.*, 1931, 201-206.
- 391a. Mumford, S. A., and Phillips, J. W. C., *J. Chem. Soc.*, 1929, 2112-2133.
392. Mundici, C. M., *Gazz. chim. ital.*, **34**, II, 114-124 (1904).
393. Munro, H. E., and Marvel, C. S., *J. Am. Chem. Soc.*, **54**, 4445-4450 (1932).
394. Murayama, Y., and Abe, K., *J. Pharm. Soc. Japan*, No. 498, 637-644 (1923); *Chem. Abs.*, **18**, 228-229 (1924).
395. Muskat, I. E., and Herrman, M., *J. Am. Chem. Soc.*, **53**, 252-260 (1931).
- 395a. Nametkin, S., and Nefontova, S., *J. Applied Chem. (U. S. S. R.)*, **6**, 248-256 (1933).
- 395b. Naves, Y. R., and Perrottet, E., *Helv. Chim. Acta*, **24**, 3-29 (1941).
396. Nef, J. U., *J. Am. Chem. Soc.*, **26**, 1549-1577 (1904).
397. Nemtsov, M. S., Nizovkina, T. V., and Soskina, E. A., *J. Gen. Chem. (U. S. S. R.)*, **8**, 1314-1324 (in French, 1324-1325) (1938).
398. Nenitzescu, C. D., and Cantuniari, I. P., *Ber.*, **65B**, 807-812 (1932).
399. —, —, *Ber.*, **66B**, 1097-1100 (1933).
400. —, Cioranescu, E., and Cantuniari, I. P., *Ber.*, **70B**, 277-283 (1937).
401. —, and Dragan, A., *Ber.*, **66B**, 1892-1900 (1933).
402. —, Isacescu, D. A., and Ionescu, C. N., *Ann.*, **491**, 210-220 (1931).
403. Newmann, F. H., *Ann.*, **302**, 236-244 (1898).
404. Nightingale, D., and Carton Jr., B., *J. Am. Chem. Soc.*, **62**, 280-283 (1940).
405. —, and Smith, L. I., Paper presented at Milwaukee Meeting of American Chemical Society, September 5-9, 1938; *J. Am. Chem. Soc.*, **61**, 101-104 (1939).
- 405a. —, Taylor, R. G., and Smelser, H. W., *J. Am. Chem. Soc.*, **63**, 258-261 (1941).
406. Nikolaev, A. A., *J. Gen. Chem. (U. S. S. R.)*, **6**, 1587-1592 (1936); *Chem. Abs.*, **31**, 2587 (1937).
407. Nikolaeva, A. F., and Puchkov, P. V., *Compt. rend. acad. sci. U. R. S. S.*, **24**, 345-346 (1939) (in English).
408. —, —, *J. Gen. Chem. (U. S. S. R.)*, **9**, 277-279 (1939).
- 408a. —, —, *Ibid.*, **9**, 2153-2155 (1939).
409. Nishida, K., and Uota, H., *J. Agr. Chem. Soc. Japan*, **11**, 489-494 (1935); *Chem. Abs.*, **29**, 6590 (1935); *Bull. Agr. Chem. Soc. Japan*, **11**, 95-100 (1935); *Chem. Zentr.*, 1936, I, 80-81.
410. —, —, *J. Agr. Chem. Soc. Japan*, **12**, 308-312 (1936); *Chem. Abs.*, **30**, 6356 (1936).
411. Norris, J. F., *Ind. Eng. Chem.*, **16**, 184 (1924).
412. —, and Ingraham, J. N., *J. Am. Chem. Soc.*, **62**, 1298-1301 (1940).
413. —, and Reuter, R., *Ibid.*, **49**, 2624-2640 (1927).
414. —, and Rubinstein, D., *Ibid.*, **61**, 1163-1170 (1939).
415. —, and Vaala, G. T., *Ibid.*, **61**, 2131-2134 (1939).
416. —, and Wood, J. E., *Ibid.*, **62**, 1428-1432 (1940).
- 416a. N. V. de Bataafsche Petroleum Maatschappij, Belgian Patent 429,747, Feb. 22, 1939.
- 416b. —, Belgian Patent 429,748, Feb. 22, 1939.
417. —, British Patent 496,676, Dec. 5, 1938.
- 417a. —, British Patent 501,896, March 7, 1939.
418. —, British Patent 509,540, July 18, 1939.
419. —, British Patent 512,408, Sept. 1, 1939.
420. —, (A. J. van Peski and H. F. J. Lorang, inventors), Dutch Patent 45,638, April 15, 1939.
- 420a. —, (W. C. B. Smithuysen, inventor), Dutch Patent 48,338, April 15, 1940.
- 420b. —, Dutch Patent 48,596, June 15, 1940; *Chem. Abs.*, **35**, 1415 (1941).
- 420c. —, Dutch Patent 48,660, June 15, 1940; *Chem. Abs.*, **35**, 1415 (1941).
- 420d. —, Dutch Patent 48,884, July 15, 1940; *Chem. Abs.*, **35**, 5134 (1941).
421. —, French Patent 823,545, Jan. 21, 1938.
- 421a. —, French Patent 841,004, May 9, 1939.
422. —, French Patent 841,979, June 2, 1939.
423. —, French Patent 842,204, June 8, 1939; *Chem. Abs.*, **34**, 4746 (1940).
424. Oberfell, G. G., and Frey, F. E., *Oil Gas J.*, **38**, No. 28, 50-51, No. 29, 70, 73, 74, 76 (1939).
425. Ogg Jr., R. A., *J. Am. Chem. Soc.*, **61**, 1946-1949 (1939).
426. —, and Priest, W. J., *J. Chem. Phys.*, **7**, 736-748 (1939).
427. Orcutt, R. M., and Bogert, M. T., *J. Org. Chem.*, **4**, 543-547 (1939).
428. Orechov, A. P., and Grinberg, R., *J. Russ. Phys.-Chem. Soc.*, **48**, 1702-1712 (1916); *Chem. Zentr.*, 1923, I, 1619-1620.
- 428a. Otto, R., and Stoffel, F., *Ber.*, **30**, 1799-1800 (1897).
- 428b. Palmer, R. C., and Bibb, C. H., (assignors to Newport Industries, Inc.), U. S. Patent 2,211,432, Aug. 13, 1940; *Chem. Abs.*, **35**, 467 (1941).
- 428c. Parks, G. S., *Chem. Rev.*, **27**, 75-83 (1940).
429. Pauling, L., in H. Gilman's "Organic Chemistry," John Wiley and Sons, Inc., New York, 1938, Vol. II, p. 1877.
430. —, *Ibid.*, pp. 1886-1887.
431. —, and Sherman, J., *J. Chem. Phys.*, **1**, 606-617 (1933).
432. —, —, *Ibid.*, **1**, 679-686 (1933).
433. —, and Wheland, G. W., *Ibid.*, **1**, 362-374 (1933).
434. Perlman, D., Davidson, D., and Bogert, M. T., *J. Org. Chem.*, **1**, 288-299 (1936).
435. Perry, D., *J. Am. Chem. Soc.*, **54**, 2918-2920 (1932).
436. Petrov, A. D., and Cheltsova, M. A., *Compt. rend. acad. sci. U. R. S. S.*, **15**, 79-84 (1937) (in English).
437. —, Meshcheryakov, A. P., and Andreev, D. N., *Ber.*, **68B**, 1-5 (1935); *J. Gen. Chem. (U. S. S. R.)*, **5**, 972-976 (1935).
438. —, and Shchukin, V., *Ibid.*, **9**, 506-508 (1939).
439. Peuffaillit, L., and Austerweil, G., French Patent 563,208, Nov. 19, 1923; *Chem. Zentr.*, 1927, II, 2115-2116.
440. Pines, H., and Ipatieff, V. N., *J. Am. Chem. Soc.*, **61**, 1076-1077 (1939).

441. —, and Ipatieff, V. N., Unpublished work dated January 1-31, 1939.
442. —, Schmerling, L., and Ipatieff, V. N., *J. Am. Chem. Soc.*, **62**, 2901-2902 (1940).
- 442a. Pitzer, K., *Chem. Rev.*, **27**, 39-57 (1940).
- 442b. Podbielniak Centrifugal Super-Contractor Co., 8312 South Chicago Avenue, Chicago, Ill., Circular 20, and Revised Circular 17.
443. Porter, C. W., "Molecular Rearrangements," The Chemical Catalog Co., Inc., (Reinhold Publishing Corp.), New York, 1928, (American Chemical Society Monograph Series No. 45).
444. —, *Ibid.*, pp. 86-87.
445. Prevost, C., *Compt. rend.*, **208**, 1589-1591 (1939).
446. Price, C. C., *J. Am. Chem. Soc.*, **61**, 1847-1849 (1939).
447. —, and Meister, M., *Ibid.*, **61**, 1595-1597 (1939).
448. Prins, H. J., *Chem. Weekblad*, **13**, 1264-1276 (1916).
449. Prokopetz, E. I., *J. Applied Chem. (U. S. S. R.)*, **7**, 159-169 (1934).
450. —, and Boguslavskaya, S. M., *Ibid.*, **11**, 847-849 (1938).
451. —, —, *Ibid.*, **11**, 1471-1474 (1938); *Foreign Petroleum Tech.*, **7**, 169-176 (1939).
452. —, and Filaretov, A. N., *Ibid.*, **11**, 1631-1635 (1938).
453. —, Pavlenko, A. V., and Boguslavskaya, S. M., *Ibid.*, **11**, 840-846 (1938).
- 453a. Prosen, E. J. R., and Rossini, F. D., *J. Research Natl. Bur. Standards*, **27**, 289-310 (1941) (Research Paper No. 1420).
- 453b. Puchkov, P. V., *J. Phys. Chem. (U. S. S. R.)*, **14**, 1319-1320 (1940).
454. —, and Nikolaeva, A. F., *J. Gen. Chem. (U. S. S. R.)*, **8**, 1153-1158 (1938).
455. —, —, *Ibid.*, **8**, 1159-1166 (1938).
456. Ramart-Lucas, P., and Amagat, P., *Bull. soc. chim. (4)*, **51**, 108-126 (1932).
457. —, —, *Compt. rend.*, **188**, 638-640 (1929).
458. —, and Salmon-Legagneur, E., *Bull. soc. chim. (4)*, **45**, 718-734 (1929).
459. Rao, B. S., and Simonsen, J. L., *J. Chem. Soc.*, 1928, 2496-2505.
- 459a. Rebner, J., (assignor to Schering-Kahlbaum A.-G.), U. S. Patent 1,967,430, July 24, 1934.
460. Reisman, J., *Bull. soc. chim. (4)*, **41**, 94-98 (1927).
461. Riban, J., *Ann. chim. phys. (5)*, **6**, 5-52 (1875).
462. —, *Ibid.*, **6**, 215-263 (1875).
463. —, *Ibid.*, **6**, 473-493 (1875).
464. —, *Compt. rend.*, **76**, 1547-1550 (1873).
465. Rice, O. K., and Gershinowitz, H., *J. Chem. Phys.*, **3**, 479-489 (1935).
466. Richter, F., and Wolff, W., *Ber.*, **59B**, 1733-1736 (1926).
467. —, —, *Ber.*, **65B**, 1714-1721 (1930).
468. Risi, J., and Gauvin, D., *Can. J. Research*, **14**, Sect. B, 255-267 (1936).
469. Robertson, J. M., Kerr, C. A., and Henderson, G. G., *J. Chem. Soc.*, 127, 1944-1946 (1925).
470. Robinson, R., and Walker, J., *Chemistry & Industry*, **13**, (54, No. 41), 906-907; **13**, (54, No. 43), 946-947 (1935).
471. Roblin Jr., R. O., Davidson, D., and Bogert, M. T., *J. Am. Chem. Soc.*, **57**, 151-159 (1935).
472. Roginski, S. Z., and Rathmann, F. H., *Ibid.*, **55**, 2800-2805 (1933).
473. Rose, A., *Ibid.*, **62**, 793-795 (1940).
- 473a. Rosenbaum, E. J., Grosse, A. V., and Jacobson, H. F., *Ibid.*, **61**, 689-692 (1939).
474. Rossander, S. S., Bock, L. H., and Marvel, C. S., *Ibid.*, **52**, 2976-2981 (1930).
475. Rossini, F. D., *J. Research Natl. Bur. Standards*, **15**, 357-361 (1935) (Research Paper No. 833).
- 475a. —, *Chem. Rev.*, **27**, 1-16 (1940).
476. —, and Knowlton, J. W., *J. Research Natl. Bur. Standards*, **19**, 249-262 (1937) (Research Paper No. 1024).
477. —, —, *J. Chem. Phys.*, **6**, 168 (1938).
- 477a. —, and Prosen, E. J. R., *J. Am. Chem. Soc.*, **62**, 2250-2251 (1940).
- 477b. —, —, and Pitzer, K. S., in Papers Presented before the Petroleum Division of the American Chemical Society, Atlantic City Meeting, Sept. 8-12, 1941, pp. 221-230; *J. Research Natl. Bur. Standards*, **27**, 529-541 (1941) (Research Paper No. 1440).
478. Roux, L., *Am. chim. phys. (6)*, **12**, 289-358 (1887).
479. Rozanov, N. A., *J. Russ. Phys.-Chem. Soc.*, **48**, 168-189 (1916).
480. —, *Ibid.*, **61**, 2291-2302 (1929).
- 480a. Rudakov, G. A., *J. Gen. Chem. (U. S. S. R.)*, **10**, 1673-1681 (1940).
481. Rupe, H., and Tomi, W., *Ber.*, **47**, 3064-3083 (1914).
482. Ruzicka, L., *Helv. Chim. Acta*, **6**, 483-492 (1923).
483. —, *Chemistry & Industry*, **13**, (54, No. 21), 509-510 (1935); cf. L. Ruzicka, W. Zimmermann, and K. Huber, *Helv. Chim. Acta*, **19**, 343-353 (1936).
484. —, and Bosch, W., *Helv. Chim. Acta*, **14**, 1336-1339 (1931).
485. —, Brugger, W., Pfeiffer, M., Schinz, H., and Stoll, M., *Ibid.*, **9**, 499-520 (1926).
486. —, and Capato, E., *Ibid.*, **8**, 259-274 (1925).
487. —, Engel, L. L., and Fischer, W. H., *Ibid.*, **21**, 364-370 (1938).
488. —, and Gibson, D. T., *Ibid.*, **14**, 570-577 (1931).
489. —, and Janot, M. M., *Ibid.*, **14**, 645-650 (1931).
490. —, Meyer, J., and Mingazzini, M., *Ibid.*, **5**, 345-368 (1922).
491. —, and Peyer, E., *Ibid.*, **18**, 676-684 (1935).
492. —, and Stoll, M., *Ibid.*, **6**, 846-855 (1923).
493. —, —, *Ibid.*, **7**, 84-94 (1924).
494. —, —, *Ibid.*, **7**, 271-282 (1924).
495. —, and van Veen, A. G., *Ann.*, **468**, 143-162 (1929).
496. Sabatier, P., and Gaudion, G., *Compt. rend.*, **168**, 670-672 (1919).
497. Sachanan, A. N., and Tilicheev, M. D., *Ber.*, **62B**, 658-677 (1929).
498. Sachse, H., *Ber.*, **22**, 1363-1370 (1890); *Z. physik. Chem.*, **10**, 203-241 (1892).
499. Salzberg, P. L., and Marvel, C. S., *J. Am. Chem. Soc.*, **50**, 1737-1744 (1928).
500. Schaarschmidt, A., *Petroleum Z.*, **28**, No. 12, 1-4 (1932); "Von den Kohlen und den Mineralölen, IV. Band: 1931," Verlag Chemie, G.m.b.H., Berlin, 1931, pp. 123-132; *Z. angew. Chem.*, **44**, 474-475 (1931).
- 500a. —, and Marder, M., *Brennstoff-Chem.*, **13**, 412-413 (1932); *Z. angew. Chem.*, **46**, 151-154 (1933).
501. Schering-Kahlbaum A.-G., British Patent 367,593, Feb. 25, 1932.
502. —, British Patent 375,395, June 27, 1932.
503. —, British Patent 391,073, April 20, 1933.

504. —, British Patent 403,451, Dec. 28, 1933.
- 504a. —, British Patent 405,306, Feb. 5, 1934.
505. —, French Patent 704,461, Oct. 29, 1930; *Chem. Abs.*, 25, 4560 (1931); *Chem. Zentr.*, 1931, II, 1756.
506. —, French Patent 704,809, Oct. 31, 1930; *Chem. Abs.*, 25, 4560 (1931); *Chem. Zentr.*, 1931, II, 1195.
507. —, French Patent 713,357, March 16, 1931.
508. —, French Patent 714,183, April 1, 1931; *Chem. Abs.*, 26, 1626 (1932).
- 508a. —, French Patent 739,770, Jan. 17, 1933.
509. —, French Patent 747,349, June 14, 1933.
510. —, German Patent 570,957, Feb. 22, 1933.
511. —, German Patent 578,569, June 15, 1933.
- 511a. —, German Patent 584,965, Sept. 27, 1933.
512. —, German Patent 597,258, May 19, 1934.
- 512a. —, German Patent 598,389, June 9, 1934.
513. —, German Patent 601,236 Aug. 11, 1934.
514. —, German Patent 610,402, March 16, 1935.
515. Schimmel and Co., Semi-Annual Report, October (1911), pp. 128-132.
516. Schlenk, W., and Bergmann, E., *Ann.*, 463, 1-322 (1928).
517. —, —, *Ann.*, 479, 58-77 (1930).
518. —, —, and Blum-Bergmann, O., *Ann.*, 479, 78-89 (1930).
519. —, and Marcus, E., *Ber.*, 47, 1664-1678 (1914).
520. Schneider, H. G. R., Ph.D. Thesis, Massachusetts Institute of Technology (1927), "Abstracts of Scientific and Technical Publications from the Massachusetts Institute of Technology," Number 1, 72-73 (January, 1928).
521. Schoeller, W., Schwenk, E., and Borgwardt, E., (assignors to Schering-Kahlbaum A.-G.), U. S. Patent 1,921,138, Aug. 8, 1933.
522. Schoepfle, C. S., and Ryan, J. D., *J. Am. Chem. Soc.*, 52, 4021-4030 (1930).
523. Scholl, R., and Mansfield, J., *Ber.*, 43, 1734-1746 (1910); see also R. Scholl, C. Seer, and R. Weitzenböck, *Ber.*, 43, 2202-2209 (1910).
524. —, and Seer, C., *Ann.*, 394, 111-177 (1912).
525. —, —, *Ber.*, 44, 1671-1674 (1911).
526. —, and Tritsch, W., *Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse, Abt. IIb*, 120, 793-814 (1911); *Monatsh.*, 32, 997-1018 (1911).
527. Schrauth, W., and Görig, K., *Ber.*, 56B, 1900-1906 (1923).
528. Schroeter, G., *Ber.*, 57B, 1990-2003 (1924).
529. —, Lichtenstadt, L., and Irineu, D., *Ber.* 51, 1587-1613 (1918).
- 529a. Schuit, G. C. A., Hoog, H., and Verheus, J., *Rec. trav. chim.*, 59, 793-810 (1940).
530. Scott, N. D., and Walker, J. F., *Ind. Eng. Chem.*, 32, 312-315 (1940).
531. Semmler, F. W., *Ber.*, 27, 2520-2521 (1894).
532. —, *Ber.*, 34, 3122-3130 (1901).
533. —, *Ber.*, 39, 4414-4428 (1906).
534. —, *Ber.*, 40, 2959-2968 (1907).
535. —, and Becker, A., *Ber.*, 46, 1814-1822 (1913).
536. —, and Jakubowicz, W., *Ber.*, 47, 2252-2259 (1914).
537. —, and Jonas, K. G., *Ber.*, 47, 2068-2082 (1914).
538. —, and Schiller, H. von, *Ber.*, 60B, 1591-1607 (1927).
539. —, and Spornitz, K. E., *Ber.*, 46, 4025-4029 (1913).
540. Serebriakova, E. K., and Frost, A. V., *J. Gen. Chem. (U. S. S. R.)*, 7, 122-130 (1937).
- 540a. Sergienko, S. R., *Bull. acad. sci. U. R. S. S., Classe sci. math. nat. Sér. chim.*, 1938, 753-759; *Chem. Abs.*, 33, 3329 (1939).
- 540b. —, *Compt. rend. acad. sci. U. R. S. S.*, 26, 73-75 (1940) (in English); *Chem. Abs.*, 34, 5418 (1940).
541. Sheffield, D. H., (assignor to Hercules Powder Co.), U. S. Patent 2,097,743, Nov. 2, 1937; *Chem. Abs.*, 32, 192 (1938).
542. —, (assignor to Hercules Powder Co.), U. S. Patent 2,097,744, Nov. 2, 1937; *Chem. Abs.*, 32, 192 (1938).
543. Sherman, J., *J. Chem. Phys.*, 2, 488-491 (1934).
544. Sherrill, M. L., Baldwin, C., and Haas, D., *J. Am. Chem. Soc.*, 51, 3034-3041 (1929).
545. —, Otto, B., and Pickett, L. W., *Ibid.*, 51, 3023-3033 (1929).
- 545a. Silchenko, E. I., *J. Applied Chem. (U. S. S. R.)*, 12, 421-427 (1939).
546. Simonsen, J. L., *Indian Forest Records*, 9, 289-306 (1922).
- 546a. Siverstev, A. P., *J. Gen. Chem. (U. S. S. R.)*, 10, 799-802 (1940); *Natl. Petroleum News*, 33, No. 10, R-68, R-70 (1941).
547. Skraup, S., and Beifuss, W., *Ber.*, 60B, 1070-1074 (1927).
548. Slobodin, Y. M., *J. Gen. Chem. (U. S. S. R.)*, 4, 778-782 (1934).
549. —, *Ibid.*, 5, 48-52 (1935).
550. —, *Ibid.*, 6, 129-136 (1936).
551. —, *Ibid.*, 6, 1806-1814 (1936).
552. —, *Ibid.*, 6, 1892-1896 (1936).
553. —, *Ibid.*, 7, 1664-1667 (1937).
554. —, *Ibid.*, 7, 2376-2380 (1937).
555. —, *Ibid.*, 9, 272-276 (1939).
556. Smakula, A., *Z. physik. Chem.*, B25, 90-98 (1934).
557. Smith, D. F., *J. Am. Chem. Soc.*, 49, 43-50 (1927).
558. Smith, L. I., and Cass, O. W., *Ibid.*, 54, 1614-1621 (1932).
- 558a. —, and Guss, C. O., *Ibid.*, 62, 2631-2635 (1940).
559. —, and Kiess, M. A., *Ibid.*, 61, 989-996 (1939).
560. —, and Lux, A. R., *Ibid.*, 51, 2994-3000 (1929).
561. —, and Perry, H. O., *Ibid.*, 61, 1411-1412 (1939).
- 561a. Smittenberg, J., Hoog, H., Moerbeek, B. H., and van der Zijden, M. J., *J. Inst. Petroleum*, 26, 294-303 (1940).
562. Sparks, W. J., and Marvel, C. S., *J. Am. Chem. Soc.*, 58, 865-870 (1936).
563. —, Peppel, W. J., and Marvel, C. S., *Ibid.*, 59, 1351-1352 (1937).
564. Stampfli, J. G., and Marvel, C. S., *Ibid.*, 53, 4057-4065 (1931).

565. Stavely, H. E., and Bergmann, W., *J. Org. Chem.*, **1**, 575-579 (1937).
- 565a. Stewart, T. D., and Hanson, M. H., *J. Am. Chem. Soc.*, **53**, 1121-1128 (1931).
566. Stobbe, H., *Ber.*, **42**, 565-568 (1909).
567. Stoermer, R., *Ber.*, **42**, 4865-4871 (1909).
568. —, and Foerster, G., *Ber.*, **52B**, 1255-1272 (1919).
569. —, and Kootz, H., *Ber.*, **61B**, 2330-2336 (1928).
570. —, and Voht, G., *Ann.*, **409**, 36-58 (1915).
571. Stratford, R., *Ann. combustibles liquides*, **4**, 83-108, 317-359 (1929).
572. Straus, F., *Ann.*, **342**, 190-265 (1905).
573. —, *Ber.*, **46**, 1051-1055 (1913).
574. —, and Lemmel, L., *Ber.*, **46**, 232-241 (1913).
- 574a. Sugden, S., *J. Chem. Soc.*, **121**, 858-866 (1922).
- 574b. —, *Ibid.*, **125**, 27-31 (1924).
- 574c. —, *Ibid.*, **125**, 1177-1189 (1924); "The Parachor and Valency," G. Routledge and Sons, Ltd., London, 1930.
- 574d. Suida, H., and Planckh, R., *Ber.*, **66B**, 1445-1454 (1933).
575. Sweet, R. S., and Marvel, C. S., *J. Am. Chem. Soc.*, **54**, 1184-1190 (1932).
- 575a. Swientoslawski, W., *Ibid.*, **42**, 1945-1951 (1920).
- 575aa. Syrkin, J., and Diatkina, M., *Acta Physicochim. U. R. S. S.*, **14**, 105-118 (1941).
- 575b. Szebellédy, L., *Z. anal. Chem.*, **81**, 36-41 (1930).
576. Tanatar, S., *Ber.*, **29**, 1297-1300 (1896); **32**, 702-705 (1899).
577. —, *Z. physik. Chem.*, **41**, 735-738 (1902).
578. Taylor, T. W. J., and Murray, A. R., *J. Chem. Soc.*, **1938**, 2078-2086.
- 578a. Temkin, M., *Acta Physicochim. U. R. S. S.*, **13**, 733-746 (1940).
579. Thiele, J., and Bühner, A., *Ann.*, **347**, 249-274 (1906).
580. —, and Henle, F., *Ann.*, **347**, 290-315 (1906).
581. Thomas, C. L., Private Communication dated Nov. 6, 1938.
- 581a. —, and Bloch, H. S., (assignors to Universal Oil Products Co.), U. S. Patent 2,216,284, Oct. 1, 1940.
- 581b. —, Egloff, G., and Morrell, J. C., *Ind. Eng. Chem.*, **29**, 1260-1267 (1937); **30**, 842 (1938).
- 581c. Thomas, M. H., and Wetmore, F. E. W., *J. Am. Chem. Soc.*, **63**, 136-137 (1941).
582. Tiemann, F., *Ber.*, **33**, 3710-3713 (1900).
583. —, and Semmler, F. W., *Ber.*, **26**, 2708-2729 (1893).
584. Tiffeneau, M., *Compt. rend.*, **139**, 481-482 (1904).
585. —, and Daudel, *Compt. rend.*, **147**, 678-680 (1908).
586. Tischenko, V. E., and Rudakov, G. A., *J. Applied Chem. (U. S. S. R.)*, **6**, 691-704 (1933).
- 586a. Todd, S. S., and Parks, G. S., *J. Am. Chem. Soc.*, **58**, 134-137 (1936).
587. Toivonen, N. J., *Suomen Kemistilehti*, **9**, 15-16, 75-76 (1936) (in German); *Chem. Zentr.*, **1936**, II, 3802-3803; *Chem. Abs.*, **31**, 2195 (1937).
588. —, Veijola, T., and Friberg, S., *Suomen Kemistilehti*, **8**, 44B-46B (1935) (in German); *Chem. Zentr.*, **1936**, I, 4012-4013; *Chem. Abs.*, **30**, 2185 (1936).
589. Tolman, R. C., *J. Am. Chem. Soc.*, **42**, 2506-2528 (1920).
590. Trautz, M., and Winkler, K., *J. prakt. Chem. (2)*, **104**, 53-79 (1922).
- 590a. Treadwell, F. P., and Hall, W. T., "Analytical Chemistry, Vol. II: Quantitative Analysis," John Wiley and Sons, Inc., New York, 1935, p. 629.
591. Treibs, W., *Ber.*, **68B**, 1751-1756 (1935).
592. Tsao, J. C., and Marvel, C. S., *J. Am. Chem. Soc.*, **55**, 4709-4713 (1933).
593. Tschitschibabin, A. E., *J. prakt. Chem. (2)*, **74**, 340-344 (1906).
- 593a. Turk, A., Abstracts of Doctoral Dissertations, No. 34, The Ohio State University Press, 1941, pp. 607-617.
594. Turova-Pollak, M. B., *J. Gen. Chem. (U. S. S. R.)*, **7**, 369-371 (1937).
- 594a. —, Sci. Reports Moscow State Univ., **3**, 193-196 (1934); *Chem. Abs.*, **30**, 8190 (1936).
595. —, and Baranovskaya, N. B., *J. Gen. Chem. (U. S. S. R.)*, **9**, 429-431 (1939).
596. —, and Koshelev, A. F., *Ibid.*, **9**, 2179-2183 (1939).
597. —, and Makaeva, Z., *Ibid.*, **9**, 1279-1282 (1939).
598. —, and Pollakova, O. I., *Ibid.*, **9**, 233-238 (1939).
- 598a. —, and Slovokhotova, T. A., *Ibid.*, **10**, 1435-1438 (1940); *Foreign Petroleum Tech.*, **9**, 28-34 (1941).
- 598aa. —, and Sidel'kovskaya, F. P., *Ibid.*, **11**, 817-820 (1941).
- 598ab. —, —, *Ibid.*, **11**, 821-823 (1941).
- 598b. —, and Tarasova, G. A., *Ibid.*, **10**, 172-175 (1940).
- 598c. —, and Vsevolozhskaya, E. V., *Ibid.*, **11**, 824-828 (1941).
599. —, and Zelinsky, N. D., *Ber.*, **68B**, 1781-1785 (1935).
600. Twigg, G. H., *Trans. Faraday Soc.*, **35**, 934-945 (1939).
- 600a. —, *Proc. Roy. Soc. London*, **A178**, 106-117 (1941).
- 600b. Ubbelohde, L., *Petroleum Z.*, **29**, No. 23, 1-24 (1933).
601. Uchida, S., *J. Am. Chem. Soc.*, **38**, 687-699 (1916).
- 601a. Ulfers, F., and Erbe, R., (assignors to Schering-Kahlbaum A.-G.), U. S. Patent 1,996,558, April 2, 1935.
602. Unger, F., *Ber.*, **65B**, 467-472 (1932).
603. Universal Oil Products Co., British Patent 498,463, Jan. 5, 1939.
604. —, British Patent 498,512, Jan. 5, 1939.
605. —, French Patent 823,595, Jan. 22, 1938.
606. Uota, H., *J. Dept. Agr., Kyushu Imp. Univ.*, **5**, 117-193 (1937); *Chem. Abs.*, **31**, 7416-7418 (1937).
607. Urushibara, Y., and Simamura, O., *Bull. Chem. Soc., Japan*, **12**, 507-509 (1937) (in English).
608. —, —, *Ibid.*, **13**, 566-569 (1938) (in English).
609. —, —, *Ibid.*, **14**, 323-336 (1939) (in English).
- 609a. van Peski, A. J., and Lorang, H. F. J., (assignors to Universal Oil Products Co.), U. S. Patent 2,220,693, Nov. 5, 1940.
- 609aa. van Risseghem, H., *Bull. soc. chim. Belg.*, **28**, 187-198 (1914).
- 609b. Vavon, G., *Bull. soc. chim. (4)*, **39**, 666-673 (1926).
- 609c. —, and Peignier, P., *Bull. soc. chim. (4)*, **39**, 924-942 (1926).
610. Venable, C. S., *J. Am. Chem. Soc.*, **45**, 728-734 (1923).
611. Vogel, A. I., *Chemistry & Industry*, **16**, (57, No. 23), 541-542 (1938); *J. Chem. Soc.*, **1938**, 1323-1338.

612. —, *Ibid.*, 16, (57, No. 33), 772-773 (1938).
613. Vorländer, D., and Siebert, C., *Ber.*, 39, 1024-1035 (1906).
614. Wagner, G., *J. Russ. Phys.-Chem. Soc.*, 31, 680-684 (1899); cf. G. Wagner and W. Brickner, *Ber.*, 32, 2302-2325 (1899).
615. Wallach, O., *Ann.*, 227, 277-302 (1885).
616. —, *Ann.*, 230, 225-272 (1885).
617. —, *Ann.*, 239, 1-54 (1887).
618. —, *Ann.*, 245, 241-278 (1888).
619. —, *Ann.*, 252, 94-105 (1889).
620. —, *Ann.*, 275, 103-110 (1893).
- 620a. —, *Ann.*, 302, 371-387 (1898).
621. —, *Ann.*, 350, 141-157 (1906).
622. —, *Ann.*, 350, 162-169 (1906).
623. —, *Ann.*, 359, 287-316 (1908).
624. —, and Churchill, J. B., *Ann.*, 360, 70-74 (1908).
625. —, *Ann.*, 363, 1-19 (1908).
626. —, *Ber.*, 39, 2504-2505 (1906).
627. —, and Churchill, J. B., *Ann.*, 360, 75-79 (1908).
628. —, —, and Rentschler, M., *Ann.*, 360, 55-59 (1908).
629. —, and Evans, E., *Ann.*, 360, 44-50 (1908).
630. —, and Fleischer, K., *Ann.*, 353, 304-309 (1907).
631. —, and Mallison, H., *Ann.*, 360, 68-70 (1908).
632. —, and Scheunert, A., *Ann.*, 324, 97-112 (1902).
633. —, and Walker, W., *Ann.*, 271, 285-299 (1892).
634. Wallis, E. S., in H. Gilman's "Organic Chemistry," John Wiley and Sons, Inc., New York, 1938, Vol. I, pp. 727-736.
635. —, *Ibid.*, pp. 799-801.
636. Washburn, E. W., Bruun, J. H., and Hicks, M. M., *J. Research Natl. Bur. Standards*, 2, 467-488 (1929) (Research Paper No. 45).
637. Waterman, H. I., Leendertse, J. J., and Cranendonk, A. C., *Rec. trav. chim.*, 58, 83-92 (1939).
638. Webel, F., U. S. Patent 1,083,164, Dec. 30, 1913.
639. —, U. S. Patent 1,083,165, Dec. 30, 1913.
640. Weizmann, C., Bergmann, E., and Haskelberg, L., *J. Chem. Soc.*, 1939, 391-397.
- 640a. Wheland, G. W., *J. Am. Chem. Soc.*, 63, 2025-2027 (1941).
641. Whitmore, F. C., *Ibid.*, 54, 3274-3283 (1932).
642. —, Fenske, M. R., Quiggle, D., Bernstein, H., Carney, T. P., Lawroski, S., Popkin, A. H., Wagner, R. B., Wheeler, W. R., and Whitaker, J. S., *Ibid.*, 62, 795-800 (1940).
643. —, and Meunier, P. L., *Ibid.*, 55, 3721-3722 (1933).
- 643a. Wibaut, J. P., Hoog, H., Langedijk, S. L., Overhoff, J., and Smittenberg, J., *Rec. trav. chim.*, 58, 329-377 (1939).
644. —, Langedijk, S. L., Smittenberg, J., and Hoog, H., *Chemistry & Industry*, 16 (57, No. 32), 753 (1938).
645. Wiegand, C., and Merkel, E., *Med. u. Chem.*, 3, 320-324 (1936); *Chem. Zentr.*, 1937, I, 567-568; *Brit. Chem. Abs.-A*, II, 1938, 478.
- 645a. Wieland, H., *Ber.*, 45, 484-493 (1912).
646. —, and Müller, C., *Ann.*, 401, 233-243 (1913).
647. Willemart, A., *Compt. rend.*, 197, 1429-1432 (1933).
648. —, *Ibid.*, 197, 1659-1661 (1933).
649. Williams, D., and Bost, R. W., *J. Chem. Phys.*, 4, 251-253 (1936).
650. Willstätter, R., and Kametaka, T., *Ber.*, 41, 1480-1486 (1908).
651. Wilson, E., *Chem. Rev.*, 21, 129-167 (1937).
652. Wislicenus, J., *Ber. K. sächs.-Ges. Wiss. Leipzig, Math.-phys. Cl.*, 52, 117-123 (1900); *Chem. Zentr.*, 1901, I, 463-464.
653. —, and Schmidt, P., *Ann.*, 313, 210-228 (1900).
654. Wittig, G., and Kosack, H., *Ann.*, 529, 167-184 (1937).
655. Wright, G. F., *J. Am. Chem. Soc.*, 61, 2106-2110 (1939).
656. Wüest, H.-M., *Ann.*, 415, 291-337 (1918).
657. Würtz, A., *Bull. soc. chim. (1)*, 5, 300-317 (1863).
658. Young, W. G., Pressman, D., and Coryell, C. D., *J. Am. Chem. Soc.*, 61, 1640-1644 (1939).
659. Yuriev, Y. K., and Pavlov, P. Y., *J. Gen. Chem. (U.S.S.R.)*, 7, 97-99 (1937); *Oil Gas J.*, 37, No. 13, 55, 57 (1938).
660. Zechmeister, L., and Tuzson, P., *Nature*, 141, 249-250 (1938).
661. —, —, *Ber.*, 72B, 1340-1346 (1939).
662. Zeitschel, O., German Patent 204,163, July 8, 1907; Friedlaender's *Fortschritte der Teerfarbenfabrikation*, 9, 1153-1154 (1911).
663. Zelinsky, N. D., *Ber.*, 44, 2783-2784 (1911).
- 663a. —, *Ber.*, 57B, 2055-2057 (1924).
- 663b. —, *Ber.*, 57B, 2058-2059 (1924).
664. —, *Ber.*, 58B, 864-869 (1925).
665. —, and Arbusov, J. A., *Compt. rend. acad. sci. U.R.S.S.*, 23, 794-798 (1939) (in English).
666. —, —, *Ibid.*, 24, 542-544 (1939) (in English).
667. —, and Freiman, M. T., *Ber.*, 63B, 1485-1488 (1930); *J. Russ. Phys.-Chem. Soc.*, 62, 1523-1528 (1930).
668. —, and Gutt, I. P., *J. Russ. Phys.-Chem. Soc.*, 38, 1289-1291 (1906).
669. —, and Levina, R. Y., *Ann.*, 476, 60-70 (1929).
- 669a. —, —, *Ber.*, 62B, 339-343 (1929).
670. —, —, *Ber.*, 62B, 1861-1863 (1929).
671. —, and Margolis, E. I., *Ber.*, 65B, 1613-1617 (1932).
- 671a. —, and Pavlov, G. S., *Ber.*, 57B, 1066-1070 (1924).
- 671b. —, —, *Ber.*, 66B, 1420-1422 (1933).
- 671c. —, and Shuikin, N. I., *Ber.*, 62B, 2180-2186 (1929).
672. —, and Stscherbak, B. A., *J. Russ. Phys.-Chem. Soc.*, 45, 379 (1913).
673. —, and Turova-Pollak, M. B., *Ber.*, 58B, 1292-1298 (1925).
674. —, —, *Ber.*, 62B, 1658-1663 (1929).

[illegible][illegible][illegible][illegible]

Author Index

A

Abe, K., 128³⁹⁴, 323³⁹⁴, 347³⁹⁴, 468³⁰⁴
 Abell, R. D., 199¹, 391¹, 461¹
 Adida, A., 119¹³³, 143¹³³, 315¹³³, 351¹³³, 463¹³³
 Adkins, 141
 Adkins, H., 44¹⁵⁰, 148¹⁵⁰, 196¹⁵⁰, 353¹⁵⁰, 389¹⁵⁰, 463¹⁵⁰
 Agejewa, M., 161², 367², 461²
 Aichner, F., 450
 Alber, E., 162¹⁸³, 367¹⁸³, 464¹⁸³
 Alder, K., 119^{2a, b}, 461^{2a, b}
 Althausen, D., 179³, 184³, 381³, 461³
 Amagat, P., 161^{456, 457}, 164⁴⁵⁶, 367^{456, 457}, 369⁴⁵⁶, 376^{456, 457}
 Andant, A., 21^{3a}, 461^{3a}
 Ando, S., 101^{4, 5, 5a}, 297^{4, 5, 5a, b}, 461^{4-5b}
 Andreev, D. N., 36⁴³⁷, 40⁴³⁷, 41⁴³⁷, 42⁴³⁷, 55⁴³⁷, 64⁴³⁷, 237⁴³⁷, 239⁴³⁷, 241⁴³⁷, 261⁴³⁷, 468⁴³⁷
 Andreevski, J., 170³³², 188³³², 377³³², 387³³², 466³³²
 Anglo-Iranian Oil Co., Ltd., 26⁵⁰, 443, 461⁵⁰
 Anon., 426, 432, 433
 Anschuetz, R., 155^{6, 7}, 357⁷, 359⁶, 361^{6, 7}, 461^{6, 7}
 Arbusov, B. A., 77⁸, 116¹², 117¹², 141^{9, 10}, 142^{8, 11}, 145¹², 281⁸, 311¹², 333^{8, 11}, 335^{8, 10, 11}, 351¹², 461⁸⁻¹²
 —, J. A., 44⁶⁶⁵, 67^{12a}, 125⁶⁶⁵, 126^{12a}, 127⁶⁶⁶, 263^{12a}, 295^{12a}, 301^{12b}, 319^{12a, 665}, 321⁶⁶⁶, 461^{12a, 12b}, 472^{665, 666}
 Armstrong, H. E., 141^{13, 14}, 343^{13, 14}, 461^{13, 14}
 Arrhenius, S., 26¹⁵, 461¹⁵
 Arveson, M. H., 456
 Asahina, Y., 119^{15a, b}, 461^{15a, b}
 Aschan, O., 28¹⁶, 63¹⁶, 99¹⁶, 119¹⁷, 143¹⁷, 257¹⁶, 297¹⁶, 299¹⁶, 461^{16, 17}
 Aston, J. G., 21^{17a}, 31³⁷⁵, 461^{17a}, 467³⁷⁵
 Atlantic Refining Co., 451
 Austerweil, G., 118^{19, 20, 21}, 119^{18, 19, 20}, 143⁴³⁹, 315^{18, 19, 20, 21}, 347²⁰, 349⁴³⁹, 461¹⁸⁻²¹, 468⁴³⁹
 Auwers, K. von, 135^{22, 23}, 136²³, 137²³, 329^{22, 23}, 461^{22, 23}

B

Bachman, G. B., 85²⁴, 287²⁴, 461²⁴
 Bachmann, W. E., 201²⁶, 208²⁵, 209²⁵, 393²⁶, 395²⁵, 461^{25, 26}
 Baddeley, G., 155²⁸, 158²⁷, 159²⁷, 357²⁸, 359²⁸, 365²⁷, 461^{27, 28}
 Badische Anilin- und Soda-Fabrik, 60³³, 64³³, 71³¹, 84^{29, 31, 32}, 257³³, 261³³, 271^{30, 31}, 287^{29, 32}, 439^{440, 448}, 461²⁹⁻³³
 Badoche, M., 197³⁴, 391³⁴, 461³⁴
 Baeyer, 18
 Baldwin, C. 61⁵⁴⁴, 257⁵⁴⁴, 470⁵⁴⁴
 Baranovskaya, N. B., 98⁵⁹⁵, 293⁵⁹⁵, 471⁵⁹⁵
 Barbier, P., 143^{35, 36}, 144^{35, 36}, 347^{35, 36}, 461^{35, 36}
 Barrett, J. W., 113³⁷, 309³⁷, 461³⁷
 Bartlett, J. H., 32^{37a}, 229^{37a}, 231^{37a}, 461^{37a}
 —, P. D., 66³⁸, 119³⁹, 461^{38, 39}
 Batt, L., 179¹⁹⁰, 464¹⁹⁰
 Bauer, O. W., 21^{39a}, 23^{39a}, 24^{39a}, 33^{39a}, 36^{39a}, 40^{39a}, 235^{39a}, 237^{39a}, 241^{39a}, 243^{39a}, 420^{39a}, 461^{39a}
 Beath, G. B., 149⁴⁰, 355⁴⁰, 461⁴⁰
 Beatty, H. A., 35⁹⁶, 36⁹⁶, 237⁹⁶, 462⁹⁶
 Becker, A., 131⁵³⁵, 325⁵³⁵, 470⁵³⁵
 Beckmann, S., 119^{319a}, 466^{319a}
 Béhal, A., 85^{41, 42}, 86⁴³, 287^{41, 42, 43}, 461⁴¹⁻⁴³
 Beifuss, W., 99⁵⁴⁷, 297⁵⁴⁷, 470⁵⁴⁷
 Belov, V. N., 170^{43a}, 377^{43a}, 461^{43a}
 Berchet, G., 197³⁸⁷, 391³⁸⁷, 468³⁸⁷
 Bergmann, E., 165⁵¹⁶, 167^{50, 517}, 168^{52, 516, 517, 518}, 170^{54, 55}, 171⁵⁷, 172⁵¹, 176⁵⁷, 188⁵⁴, 193^{57a}, 194⁴⁴, 195^{44, 640}, 196^{47, 58}, 197⁶⁴⁰, 202⁴⁹, 203⁴⁸, 207^{45, 47}, 211⁴⁶, 213⁵⁶, 369⁵¹⁶, 375^{50, 517}, 377^{52, 53, 54, 55, 57}, 377^{516, 518}, 379^{51, 57}, 381⁵⁷, 389^{44, 47, 57a, 58, 640}, 393⁴⁹, 395⁴⁵, 397⁴⁶, 399⁵⁶, 427⁴⁶¹⁻⁵¹, 462⁵²⁻⁵⁸, 470⁵¹⁶⁻⁵¹⁸, 472⁶⁴⁰

Bergmann, F., 196^{47, 58}, 203⁴⁸, 207⁴⁷, 389^{47, 58}, 431^{461-47, 48}, 462⁵⁸
 —, W., 150⁵⁶⁵, 355⁵⁶⁵, 471⁵⁶⁵
 Berkman, S., 8, 21^{58a}, 462^{58a}
 Bernstein, H., 64⁶⁴², 472⁶⁴²
 Bernthsen, W., 187⁵⁹, 387⁵⁹, 462⁵⁹
 Berthelot, M. P. E., 95⁶², 140⁶⁰, 156^{61, 63}, 291⁶², 331⁶⁰, 361^{61, 63}, 462⁶⁰⁻⁶³
 Berthoud, A., 57⁶⁴, 462⁶⁴
 Bertram, J., 146⁶⁵, 147⁶⁵, 462⁶⁵
 Beynon, J. H., 443
 Bibb, C. H., 44^{428b}, 468^{428b}
 Bilham, P., 151^{65a}, 355^{65a}, 430^{65a}, 462^{65a}
 Birch, S. F., 41^{65b, c}, 443^{65b, c}, 462^{65b, c}
 Blackie, W. J., 151⁶⁶, 355⁶⁶, 462⁶⁶
 Blair, C. M., 22²⁴⁷, 23⁶⁷, 54^{248, 249}, 82¹¹⁰, 462⁶⁷, 463¹¹⁰, 465^{247, 248, 249}
 Bloch, H. S., 8, 24^{68a}, 59¹⁵⁸, 60^{158, 581a}, 68¹⁵⁸, 69^{158, 581a}, 89⁶⁸, 253^{581a}, 265^{158, 581a}, 267¹⁵⁸, 452^{462-68, 68a}, 463¹⁵⁸, 471^{581a}
 Blum-Bergmann, O., 168⁵¹⁸, 186⁶⁹, 202⁴⁹, 377⁵¹⁸, 385⁶⁹, 393⁴⁹, 461⁴⁹, 462⁶⁹, 470⁵¹⁸
 Bock, L. H., 200⁴⁷⁴, 391⁴⁷⁴, 469⁴⁷⁴
 Bode, H., 119^{69a}, 462^{69a}
 Böeseken, J., 44^{70, 71}, 119^{71a}, 462^{70-71a}
 Bogert, M. T., 134^{71aa, 71b, 71c}, 162^{72, 73}, 163^{73, 471}, 203⁴³⁴, 204⁴²⁷, 367^{72, 73, 471}, 369^{73, 471}, 393^{427, 434}, 462^{71aa-73}, 468^{427, 434}, 469⁴⁷¹
 Boguslavskaya, S. M., 122⁴⁵¹, 123⁴⁵¹, 193^{450, 453}, 317⁴⁵¹, 389^{450, 453}, 469^{450, 451, 453}
 Bollman, H. T., 73²⁶², 110²⁶², 161²⁶², 275²⁶², 305²⁶², 367²⁶², 465²⁶²
 Bondi, A., 167⁵⁰, 375⁵⁰, 461⁵⁰
 Borgmann, I., 109¹⁸¹, 126¹⁸¹, 305¹⁸¹, 319¹⁸¹, 464¹⁸¹
 Borgwardt, E., 126⁵²¹, 321⁵²¹, 470⁵²¹
 Bosch, W., 131⁴⁸⁴, 325⁴⁸⁴, 469⁴⁸⁴
 Bost, R. W., 70⁶⁴⁹, 472⁶⁴⁹
 Bouchardat, G., 143^{75, 76}, 144^{74, 75, 76, 77, 78}, 345⁷⁸, 347^{74, 75, 78}, 349⁷⁶, 462⁷⁴⁻⁷⁸
 Bouis, M., 71⁷⁹, 72⁷⁹, 269⁷⁹, 271⁷⁹, 462⁷⁹
 Bourguet, M., 85⁸¹, 86⁸¹, 111^{81, 83}, 180^{80, 81, 82}, 287⁸¹, 305^{81, 83}, 307^{81, 83}, 383^{80, 81}, 462⁸⁰⁻⁸³
 Bragg, L. B., 21^{83a}, 462^{83a}
 Brand, K., 181^{84, 85, 86}, 383^{84, 85, 86}, 462^{84, 85, 86}
 Brandt, C. W., 149⁸⁷, 150⁸⁷, 151⁸⁷, 355⁸⁷, 462⁸⁷
 Braun, J. von, 186⁸⁸, 385⁸⁸, 462⁸⁸
 Bredt, J., 145⁸⁹, 462^{88a, 89}
 Brickner, W., 119⁶¹⁴, 143⁶¹⁴, 472⁶¹⁴
 Briggs, L. H., 149⁹⁰, 150^{90, 90a}, 151⁹⁰, 355^{90, 90a}, 462^{90, 90a}
 British and Continental Camphor Co., Ltd., 143⁹¹, 333⁹¹, 335⁹¹, 462⁹¹
 Brockway, L. O., 56⁹², 462⁹²
 Brooks, B. T., 95²²⁴, 465²²⁴
 —, D. B., 261^{92a}, 462^{92a}
 —, L. A., 429
 Brugger, W., 107⁴⁸⁵, 469⁴⁸⁵
 Brunner, H., 66⁹³, 462⁹³
 Bruun, J. H., 21^{94, 94a, 636}, 462^{94, 94a}, 472⁶³⁶
 Bühner, A., 187⁵⁷⁹, 385⁵⁷⁹, 471⁵⁷⁹
 Buret, R., 197¹⁴³, 391¹⁴³, 463¹⁴³
 Burk, R. E., 29⁹⁵, 462⁹⁵
 Burnop, V. C. E., 44^{95b}, 197^{95a}, 389^{95a}, 391^{95a}, 462^{95a, 95b}

C

Caesar, P. D., 41^{95c}, 237^{95c}, 239^{95c}, 462^{95c}
 Calingaert, G., 35^{96, 97}, 36⁹⁶, 237^{96, 97}, 462^{96, 97}
 Campbell, K. N., 21^{97a}, 462^{97a}
 Cantuniani, I. P., 94³⁹⁸, 98³⁹⁹, 100³⁹⁹, 102⁴⁰⁰, 293³⁹⁹, 299³⁹⁹, 301⁴⁰⁰, 468³⁹⁸⁻⁴⁰⁰
 Capato, E., 78⁴⁸⁶, 79⁴⁸⁶, 281⁴⁸⁶, 469⁴⁸⁶
 Carlson, G. H., 140¹¹², 331¹¹², 463¹¹²
 Carney, T. P., 64⁶⁴², 472⁶⁴²
 Carr, E. P., 56⁹⁹, 61⁹⁸, 257⁹⁸, 462^{98, 99}
 Carrie, M. S., 149¹⁰⁰, 462¹⁰⁰

- Carter, F. D., 138¹⁰¹, 462¹⁰¹
 —, G. P., 133¹⁰², 325¹⁰², 327¹⁰², 463¹⁰²
 —, J. M., 61³⁵⁷, 467³⁵⁷
 —, P. G., 128¹⁰³, 135¹⁰³, 140¹⁰³, 323¹⁰³, 329¹⁰³, 343¹⁰³, 463¹⁰³
 Carton, Jr., B., 157⁴⁰⁴, 363⁴⁰⁴, 468⁴⁰⁴
 Cass, O. W., 156⁵⁵⁸, 361⁵⁵⁸, 363⁵⁵⁸, 470⁵⁵⁸
 Chambers, T. S., 95¹⁰⁴, 291¹⁰⁴, 463¹⁰⁴
 Charlton, R. W., 140¹⁰⁵, 143¹⁰⁵, 331¹⁰⁵, 335¹⁰⁵, 343¹⁰⁵, 345¹⁰⁵, 463¹⁰⁵
 Cheltsova, M. A., 23⁴³⁶, 65⁴³⁶, 68⁴³⁶, 261⁴³⁶, 265⁴³⁶, 468⁴³⁶
 Cheney, H., 31^{135a}, 49^{135a}, 225^{135a}, 463^{135a}
 Chernyak, M. I., 44³⁴⁰, 467³⁴⁰
 Christ, R. E., 81²⁶³, 85²⁶³, 287²⁶³, 465²⁶³
 Churchill, J. B., 110^{627, 628}, 111⁶²⁴, 305^{624, 627, 628}, 472^{624, 627, 628}
 Cioranescu, E., 102⁴⁰⁰, 301⁴⁰⁰, 468⁴⁰⁰
 Clark, W. M., 6
 Clemo, G. R., 174¹⁰⁶, 379¹⁰⁶, 463¹⁰⁶
 Clover, A. M., 128^{107, 108}, 323^{107, 108}, 463^{107, 108}
 Coffman, D. D., 82¹¹⁰, 83¹⁰⁹, 463^{109, 110}
 Cohen Henriques, P., 102¹¹¹, 463¹¹¹
 Conant, J. B., 140¹¹², 331¹¹², 463¹¹²
 Cook, J. W., 44¹²¹, 201^{116, 117}, 202¹¹⁷, 203^{114, 116, 118, 120}, 204¹²¹, 205^{113, 117, 121}, 206^{115, 123}, 207^{117, 119}, 208²⁵, 209^{25, 119}, 210^{117, 119, 122, 124}, 211¹¹³, 393^{114, 116, 117, 118}, 393^{120, 121}, 395^{25, 113, 115, 117, 119, 121, 123}, 397^{113, 117, 119}, 397^{122, 124}, 461²⁵, 463¹¹³⁻¹²⁴
 Copp, F. C., 138¹⁰¹, 462¹⁰¹
 Corson, B. B., 44¹²⁵, 463¹²⁵
 Coryell, C. D., 55⁶⁵⁸, 472⁶⁵⁸
 Coulthurst, L. J., 433
 Courtot, C., 186^{126, 127}, 385^{126, 127, 230}, 463^{126, 127}, 465²³⁰
 Cowan, D. M., 102¹²⁸, 301¹²⁸, 463¹²⁸
 Cox, M. V., 97¹²⁹, 293¹²⁹, 463¹²⁹
 Crafton, Jr., H. C., 261^{92a}, 462^{92a}
 Crafts, J. M., 29, 33, 35, 94¹⁹⁵, 154¹⁹⁶, 190, 415, 431, 444, 447, 449, 458, 464^{195, 196}
 Cramer, P. L., 66¹³⁰, 261¹³⁰, 463¹³⁰
 Cranendonk, A. C., 122⁶³⁷, 317⁶³⁷, 472⁶³⁷
 Croessmann, F., 188⁶⁷⁸, 387⁶⁷⁸, 473⁶⁷⁸
 Cross, P. C., 56⁹², 462⁹²

D

- Daniels, F., 26¹³¹, 463¹³¹
 Dansi, A., 205¹¹³, 211¹¹³, 395¹¹³, 397¹¹³, 463¹¹³
 Darkis, F. R., 61³⁰², 253³⁰², 255³⁰², 466³⁰²
 Daudel, 191⁵⁸⁵, 387⁵⁸⁵, 471⁵⁸⁵
 Davidson, D., 162^{72, 73}, 163^{73, 471}, 199^{131a}, 203⁴³⁴, 367^{72, 73, 471}, 369^{73, 471}, 391^{131a}, 393⁴³⁴, 462^{72, 73}, 463^{131a}, 468⁴³⁴, 469⁴⁷¹
 Davies, G. F., 114^{131b}, 427, 463^{131b}
 Davis, D. W., 81¹³², 87¹³², 289¹³², 463¹³²
 Day, A. R., 140¹⁰⁵, 143¹⁰⁵, 331¹⁰⁵, 335¹⁰⁵, 343¹⁰⁵, 345¹⁰⁵, 463¹⁰⁵
 Delépine, M., 119¹³³, 140^{133a}, 143^{133, 133a}, 315¹³³, 347^{133a}, 349^{133a}, 351¹³³, 463^{133, 133a}
 Demjanov, N. J., 70²³⁹, 108^{134, 238}, 269²³⁹, 305²³⁸, 463¹³⁴, 465^{238, 239}
 Denisenko, Y. I., 201^{134a}, 393^{134a}, 463^{134a}
 Desgrez, A., 86¹³⁵, 287¹³⁵, 463¹³⁵
 De Simo, M., 31^{135a}, 49^{135a}, 225^{135a}, 463^{135a}
 Desreux, V., 76¹⁴⁷, 142¹⁴⁸, 279¹⁴⁷, 333¹⁴⁸, 463^{147, 148}
 Deussen, E., 146^{136, 137}, 353^{136, 137}, 463^{136, 137}
 Deville, S.-C., 141¹³⁸, 463¹³⁸
 Diatkina, M., 26^{575aa}, 190^{575aa}, 471^{575aa}
 Dobrianski, A. F., 155¹³⁹, 357¹³⁹, 359¹³⁹, 463¹³⁹
 Dode, M., 56³⁶², 467³⁶²
 Dojarenko, M. N., 96¹⁴⁰, 108^{134, 140, 187, 238}, 293¹⁴⁰, 305^{140, 187, 238}, 463^{134, 140}, 464¹⁸⁷, 465²³⁸
 Dolliver, M. A., 62^{140a}, 463^{140a}
 D'Ouville, E. L., 456, 457, 458
 Dowgelewitsch, N., 99²⁷⁵, 295²⁷⁵, 465²⁷⁵
 Dragan, A., 33⁴⁰¹, 35⁴⁰¹, 235⁴⁰¹, 237⁴⁰¹, 468⁴⁰¹
 Drake, N. L., 211¹⁴¹, 212¹⁴¹, 397¹⁴¹, 463¹⁴¹
 Dubosc, A., 84^{141a}, 285^{141a}, 463^{141a}
 Dufraisse, C., 182³⁸⁹, 183³⁸⁹, 197^{142, 143, 387, 388}, 463^{142, 143}, 468³⁸⁷⁻³⁸⁹
 Dulou, R., 76¹⁴⁷, 142^{144, 145, 146, 148}, 279¹⁴⁷, 333^{144, 145}, 333¹⁴⁸, 463¹⁴⁴⁻¹⁴⁸
 Dunstan, A. E., 41^{65b, 65c}, 95²²⁴, 462^{65b, 65c}, 465²²⁴
 Dupont, G., 76¹⁴⁷, 140¹⁴⁹, 141¹⁴⁹, 142^{144, 145, 146, 148}, 143¹⁴⁹, 279¹⁴⁷, 333^{144, 145, 148}, 343¹⁴⁹, 463¹⁴⁴⁻¹⁴⁹

- Durland, J. R., 44¹⁵⁰, 148¹⁵⁰, 196¹⁵⁰, 353¹⁵⁰, 389¹⁵⁰, 463¹⁵⁰
 Dvorkovitz, V., 129^{275a}, 323^{275a}, 465^{275a}

E

- Eby, L. T., 21^{97a}, 462^{97a}
 Eck, J. C., 150^{150a}, 355^{150a}, 430, 463^{150a}
 Egloff, G., 8, 21, 21^{58a, 151, 155, 159}, 26¹⁶⁰, 28¹⁵⁵, 29^{160, 232}, 37^{159a}, 41¹⁵², 56¹⁵³, 59^{153, 581b}, 60¹⁵⁸, 61¹⁵⁴, 68¹⁵⁸, 69¹⁵⁸, 81¹⁵⁶, 122¹⁵⁷, 155¹⁶⁰, 201¹⁶⁰, 247¹⁵⁸, 253¹⁵⁸, 265¹⁵⁸, 267¹⁵⁸, 433, 462^{58a}, 463¹⁵¹⁻¹⁶⁰, 465²³², 471^{581b}
 Egorova, V., 110¹⁶¹, 111¹⁶¹, 305¹⁶¹, 463¹⁶¹
 Eijkman, J. F., 122¹⁶², 317¹⁶², 463¹⁶²
 Eisenlohr, F., 21^{162a}, 464^{162a}
 Elliott, G. H., 197^{95a}, 391^{95a}, 462^{95a}
 El Ridi, M. S., 133^{210, 211}, 325^{210, 211}, 327^{210, 211}, 464^{210, 211}
 Eltekov, A., 63¹⁶³, 71¹⁶⁴, 464^{163, 164}
 Elyashberg, I. A., 164^{342a}, 191^{342a}, 369^{342a}, 387^{342a}, 467^{342a}
 Enderlin, L., 197^{165, 388}, 391^{165, 388}, 464¹⁶⁵, 468³⁸⁸
 Engel, L. L., 147⁴⁸⁷, 469⁴⁸⁷
 —, W. F., 29^{165a}, 221^{165a}, 223^{165a}, 225^{165a}, 446, 464^{165a}
 Engler, C., 55¹⁶⁶, 245¹⁶⁶, 464¹⁶⁶
 Enklaar, C. J., 76^{167, 168}, 77^{167, 169}, 281^{167, 169}, 464¹⁶⁷⁻¹⁶⁹
 Erbe, R., 143^{601a}, 339^{601a}, 341^{601a}, 450, 471^{601a}
 Errington, K. D., 127¹⁷⁰, 131³⁵³, 145³⁵³, 323^{170, 353}, 351³⁵³, 464¹⁷⁰, 467³⁵³
 Ertchikovski, G., 144¹⁷¹, 347¹⁷¹, 464¹⁷¹
 Evans, E., 109⁶²⁹, 305⁶²⁹, 472⁶²⁹
 Evering, B. L., 453, 454, 456, 457, 458
 Ewell, R. H., 26¹⁷², 60^{172a}, 61^{172a}, 62^{172a}, 253^{172a}, 255^{172a}, 257^{172a}, 259^{172a}, 427, 464^{172, 172a}
 Eyring, H., 26^{173, 174, 216a}, 464^{173, 174, 216a}

F

- Farley, E. D., 179¹⁷⁵, 184¹⁷⁵, 381¹⁷⁵, 464¹⁷⁵
 Farmer, E. H., 66⁹³, 462⁹³
 Faworsky, A., 70¹⁷⁹, 71^{176, 177}, 72¹⁸², 74¹⁷⁹, 75¹⁷⁹, 81^{178, 180}, 82^{176, 180}, 84^{176, 177, 180}, 85^{176, 177, 180}, 86¹⁷⁹, 89, 109¹⁸¹, 126¹⁸¹, 269¹⁷⁹, 271^{176, 182}, 277¹⁷⁹, 279¹⁷⁹, 285^{176, 177, 178, 180}, 287^{176, 177, 179, 180}, 305¹⁸¹, 319¹⁸¹, 464¹⁷⁶⁻¹⁸²
 Feldman, J., 199^{131a}, 391^{131a}, 463^{131a}
 Fenske, M. R., 64⁶⁴², 472⁶⁴²
 Ferrari, O., 427
 Fichter, F., 162¹⁸³, 179¹⁸⁴, 367¹⁸³, 464^{183, 184}
 Fidler, A. E., 41^{65c}, 462^{65c}
 Fieser, L. F., 190^{184a}, 191¹⁸⁵, 206¹⁸⁶, 387¹⁸⁵, 395¹⁸⁶, 464^{184a, 185, 186}
 Filaretov, A. N., 98⁴⁵², 101⁴⁵², 293⁴⁵², 297⁴⁵², 469⁴⁵²
 Filipov, O., 108¹⁸⁷⁻¹⁸⁹, 305^{187, 189}, 464¹⁸⁷⁻¹⁸⁹
 Finlay, H. J., 149³⁶⁷, 355³⁶⁷, 467³⁶⁷
 Fischer, 141
 Fischer, W. H., 147⁴⁸⁷, 469⁴⁸⁷
 Fittig, R., 179¹⁹⁰, 464¹⁹⁰
 Flavitsky, F., 141¹⁹¹, 345¹⁹¹, 464¹⁹¹
 Fleischer, K., 109⁶³⁰, 305⁶³⁰, 472⁶³⁰
 Flood, D. T., 35⁹⁷, 237⁹⁷, 462⁹⁷
 Foerster, G., 199⁵⁶⁸, 391⁵⁶⁸, 471⁵⁶⁸
 Ford, J. H., 183¹⁹², 464¹⁹²
 Forney, W. E., 453
 Francis, A. W., 41^{95c}, 237^{95c}, 239^{95c}, 462^{95c}
 Frank, E., 119^{257c}, 465^{257c}
 Franke, N. W., 30^{384, 385}, 31³⁸⁴, 32³⁸⁵, 33³⁸⁵, 49^{384, 385}, 219^{384, 385}, 229^{384, 385}, 233³⁸⁵, 235³⁸⁵, 467³⁸⁴, 468³⁸⁵
 Freiman, M. T., 106⁶⁶⁷, 303⁶⁶⁷, 472⁶⁶⁷
 Freudenberg, K., 167³²⁴, 466³²⁴
 Frey, F. E., 26^{193, 194, 424}, 464^{193, 194}, 468⁴²⁴
 Friberg, S., 121⁵⁸⁸, 471⁵⁸⁸
 Friedel, C., 29, 33, 35, 94¹⁹⁵, 154¹⁹⁶, 190, 415, 431, 444, 447, 449, 458, 464^{195, 196}
 Friedman, B., 8
 Friedmann, W., 28¹⁹⁷, 41¹⁹⁷, 42¹⁹⁷, 239¹⁹⁷, 464¹⁹⁷
 Frost, A. V., 24, 24^{193a}, 27^{193a}, 31¹⁹⁸, 58^{199, 200}, 59^{199, 540}, 249^{199, 200}, 251^{200, 540}, 253^{199, 200, 540}, 257²⁰⁰, 267²⁰⁰, 450, 464¹⁹³⁻²⁰⁰, 470⁵⁴⁰
 Fujita, Y., 116²⁰¹, 143²⁰², 311²⁰¹, 331²⁰², 333²⁰², 464^{201, 202}
 Fussteig, R., 55²⁰³, 245²⁰³, 464²⁰³

G

- Gachard, R., 140¹⁴⁹, 141¹⁴⁹, 143¹⁴⁹, 343¹⁴⁹, 463¹⁴⁹
 Gadzjacki, V. T., 73²⁰⁴, 118²⁰⁴, 464²⁰⁴
 Gallas, G., 333^{204a}, 464^{204a}
 Ganapathi, K., 112²⁰⁵, 464²⁰⁵
 Gaponenkov, T. K., 333²⁰⁶, 464²⁰⁶
 Gascoigne, R. M., 135^{206a, b}, 139^{206a, b}, 140^{206b},
 329^{206b}, 331^{206b}, 464^{206a, b}
 Gaudion, G., 142⁴⁹⁶, 469⁴⁹⁶
 Gauvin, D., 169⁴⁶⁸, 377⁴⁶⁸, 469⁴⁶⁸
 Gaverdovskaya - Yuschkevitch, M. V., 159²⁰⁷,
 464²⁰⁷
 Genvresse, P., 128^{208, 209}, 140^{208, 209}, 323^{208, 209},
 341^{208, 209}, 464^{208, 209}
 Gercke, A., 119^{257c}, 465^{257c}
 Gershinowitz, H., 95⁴⁶⁵, 469⁴⁶⁵
 Gibson, D. T., 146⁴⁸⁸, 353⁴⁸⁸, 469⁴⁸⁸
 Gilbert, E. C., 114^{131b}, 427⁴⁶³, 463^{131b}
 Gillam, A. E., 133^{102, 210, 211}, 325^{102, 210, 211}, 327^{102, 210},
 327²¹¹, 463¹⁰², 464^{210, 211}
 Gillet, A., 56²¹², 245²¹², 464²¹²
 Gilman, H., 26^{429, 430}, 27⁶³⁴, 66⁶³⁵, 95²¹³, 464²¹³,
 468^{429, 430}, 472^{634, 635}
 Ginzburg, Y. I., 173²¹⁴, 379²¹⁴, 464²¹⁴
 Glasebrook, A. L., 31²¹⁶, 66¹³⁰, 98²¹⁵, 100²¹⁵, 101²¹⁵,
 229²¹⁶, 231²¹⁶, 261¹³⁰, 293²¹⁵, 299²¹⁵, 463¹³⁰,
 464^{215, 216}
 Glasstone, S., 26^{216a}, 464^{216a}
 Goebel, M. T., 179²¹⁷, 183²¹⁷, 465²¹⁷
 Goerig, K., 106⁵²⁷, 470⁵²⁷
 Goldblatt, L. A., 117^{217b}, 142^{217a}, 311^{217b}, 331^{217a},
 429⁴⁶⁵, 465^{217a, b}
 Goldsby, A. R., 55²⁶⁴, 58²⁶⁴, 60²⁶⁵, 245²⁶⁴, 247²⁶⁴,
 253²⁶⁵, 465^{264, 265}
 Goldwasser, S., 27^{219, 220}, 44^{219, 221}, 64²²⁰, 66²²⁰, 67²²⁰,
 259²²⁰, 261²²⁰, 263²²⁰, 465²¹⁸⁻²²¹
 Golmov, V. P., 426
 Golub, G. B., 44³⁴¹, 467³⁴¹
 Gomberg, M., 159^{222, 223}, 365²²², 465^{222, 223}
 Goodyear, G. H., 60²⁶⁵, 253²⁶⁵, 465²⁶⁵
 Gould, D. W., 95²²⁴, 465²²⁴
 Goulden, F., 210¹²⁴, 397¹²⁴, 463¹²⁴
 Graebe, C., 192²²⁵, 389²²⁵, 465²²⁵
 Gresham, T. L., 62^{140a}, 463^{140a}
 Grignard, V., 40²²⁸, 77²²⁷, 78²²⁶, 103²²⁸, 143^{35, 36},
 144^{35, 36}, 177²²⁹, 281^{226, 227}, 347^{35, 36}, 381²²⁹,
 461^{35, 36}, 465²²⁶⁻²²⁹
 Grinberg, R., 186⁴²⁸, 385^{230, 428}, 465²³⁰, 468⁴²⁸
 Griner, G., 73²³¹, 86²³¹, 275²³¹, 465²³¹
 Groot, de M., 44⁷⁰, 462⁷⁰
 Grosse, A. V., 21^{473a}, 26^{277, 278}, 28²⁷⁶, 29^{232, 276}, 31²⁷⁶,
 33²⁷⁶, 40^{232a}, 94²⁸¹, 221²⁷⁶, 233^{232a}, 235²⁷⁶,
 465^{232, 232a, 276}, 466^{277, 278, 281}, 469^{473a}
 Groth, P., 159²³³, 465²³³
 Guest, H. H., 85²³⁴, 287²³⁴, 465²³⁴
 Gugelmann, W., 134²⁹⁷, 327²⁹⁷, 466²⁹⁷
 Gurvitch, L. G., 143^{235, 236}, 335^{235, 236}, 465^{235, 236}
 Guss, C. O., 158^{558a}, 365^{558a}, 470^{558a}
 Gustavson, G., 70²³⁹, 108^{187, 237, 238}, 269²³⁹, 305^{187, 238},
 459⁴⁶⁴, 464¹⁸⁷, 465²³⁷⁻²³⁹
 Gutt, I. P., 109⁶⁶⁸, 305⁶⁶⁸, 472⁶⁶⁸
 Györy, 408^{590a}

H

- Haas, D., 61⁵⁴⁴, 257⁵⁴⁴, 470⁵⁴⁴
 Hall, W. T., 471^{590a}
 Halley, L. F., 179²⁴⁰, 182²⁴⁰, 183²⁴⁰, 383²⁴⁰, 465²⁴⁰
 Han, K., 148³⁶³, 149^{363, 364}, 467^{363, 364}
 Hanson, M. H., 415^{565a}, 471^{565a}
 Hardy, P. E., 60^{172a}, 61^{172a}, 62^{172a}, 253^{172a}, 255^{172a},
 257^{172a}, 259^{172a}, 427⁴⁶⁴, 464^{172a}
 Harkness, R. W., 58²⁴¹, 465²⁴¹
 Harmon, J., 185²⁴², 385²⁴², 465²⁴²
 Harries, C., 78²⁴³, 281²⁴³, 465²⁴³
 Haskelberg, L., 195⁶⁴⁰, 197⁶⁴⁰, 389⁶⁴⁰, 472⁶⁴⁰
 Haslewood, G. A. D., 203¹¹⁴, 206¹¹⁵, 393¹¹⁴, 395¹¹⁵,
 463^{114, 115}
 Heilbron, I. M., 79²⁴⁴, 281²⁴⁴, 465²⁴⁴
 Heise, R., 155²⁴⁵, 156²⁴⁵, 357²⁴⁵, 359²⁴⁵, 361²⁴⁵,
 465²⁴⁵
 Helfenstein, A., 80²⁹⁵, 466²⁹⁵
 Henderson, G. G., 146⁴⁶⁹, 147²⁴⁶, 148⁴⁶⁹, 353^{246, 469},
 465²⁴⁶, 469⁴⁶⁹
 Henle, F., 189⁵⁸⁰, 387⁵⁸⁰, 471⁵⁸⁰

- Henze, H. R., 22²⁴⁷, 23⁰⁷, 54^{248, 249}, 82¹¹⁰, 462⁴⁶³,
 463¹¹⁰, 465^{247, 248, 249}
 Hepp, H. J., 26¹⁹⁴, 464¹⁹⁴
 Hercules Powder Co., 141^{541, 542}, 343⁵⁴², 470^{541, 542}
 Herrman, M., 175³⁹⁵, 381³⁹⁵, 468³⁹⁵
 Hershberg, E. B., 191¹⁸⁵, 387¹⁸⁵, 464¹⁸⁵
 Hewett, C. L., 201^{116, 117}, 202¹¹⁷, 203^{116, 118, 120, 250},
 205^{113, 117}, 206²⁵⁰, 207^{117, 119}, 208²⁵, 209^{25, 119},
 210^{117, 119}, 211¹¹³, 393^{116, 117, 118, 120}, 395^{25, 113, 117, 119},
 395²⁵⁰, 397^{113, 117, 119}, 461²⁵, 463^{113, 116-120}, 465²⁵⁰
 Hibben, J. H., 21²⁵¹, 465²⁵¹
 Hibbit, D. C., 114²⁵², 131²⁵³, 309²⁵², 325²⁵³,
 465^{252, 253}
 Hicks, M. M., 21⁶³⁶, 472⁶³⁶
 Hill, A. J., 85²⁴, 287²⁴, 461²⁴
 Himel, C. M., 44^{358b, c}, 359⁴⁶⁷, 358b, c, 359
 Hirao, N., 140^{254, 255}, 141²⁵⁵, 143^{255, 256}, 341^{255, 256},
 343^{254, 255}, 465²⁵⁴⁻²⁵⁶
 Hirsch, S., 179¹⁸⁴, 464¹⁸⁴
 Hollingsworth, E. W., 150^{150a}, 355^{150a}, 430⁴⁶³, 463^{150a}
 Holm, M. M., 452
 Hoog, H., 21^{643a}, 31^{135a, 529a}, 32^{529a}, 33^{529a}, 34^{529a},
 37^{561a}, 38^{561a}, 49^{135a, 529a}, 59^{529a}, 60^{257a}, 63^{529a},
 65^{257a, 529a}, 69^{257a, 561a}, 98^{529a}, 100^{529a}, 102^{529a, 644},
 103^{529a}, 126^{529a}, 225^{135a, 529a}, 227^{529a}, 233^{529a},
 235^{529a}, 237^{529a}, 249^{257a, 529a}, 253²⁵⁷, 257^{257a},
 259^{529a}, 261^{257a, 529a}, 265^{257a, 561a}, 267²⁵⁷, 293^{529a},
 299^{529a, 643a}, 301^{529a}, 303^{529a}, 319^{529a}, 439⁴⁴⁶,
 463^{135a}, 465^{257, 257a}, 470^{529a, 561a}, 472^{643a, 644}
 Houben, J., 407^{257b}, 465^{257b}
 Houghton, A. S., 182³⁸⁹, 183³⁸⁹, 468³⁸⁹
 Howard, F. L., 261^{92a}, 462^{92a}
 Huber, K., 146⁴⁸³, 469⁴⁸³
 Hueckel, W., 119^{257c, 258a}, 126²⁵⁸, 127^{258a}, 321^{258, 258a},
 465^{257c, 258, 258a}
 Hugel, G., 68²⁵⁹, 263²⁵⁹, 465²⁵⁹
 Huhn, W., 95²⁷⁹, 96²⁷⁹, 97²⁷⁹, 291²⁷⁹, 293²⁷⁹, 466²⁷⁹
 Hull, C. M., 452
 Hulla, G., 8, 26¹⁶⁰, 29^{160, 232}, 155¹⁶⁰, 201¹⁶⁰, 463¹⁶⁰,
 465²³²
 Humble Oil and Refining Co., 26⁵⁰, 461⁵⁰
 Hunter, W. H., 26²⁶⁰, 465²⁶⁰
 Hurd, C. D., 55²⁶⁴, 58²⁶⁴, 60^{261, 265}, 73^{261, 262},
 81^{263, 370a}, 85²⁶³, 110²⁶², 161^{261, 262}, 245²⁶⁴, 247²⁶⁴,
 253^{261, 265}, 275^{261, 262}, 285^{370a}, 287²⁶³, 305²⁶²,
 367^{261, 262}, 465²⁶¹⁻²⁶⁵, 467^{370a}
 Huzisiro, R., 428

I

- Iball, J., 205¹¹³, 208²⁵, 209²⁵, 211¹¹³, 395^{25, 113},
 397¹¹³, 461²⁵, 463¹¹³
 I. G. Farbenindustrie, A.-G., 55^{266, 267}, 56^{266, 267},
 245^{266, 267}, 440^{443, 449}, 452⁴⁶⁵, 465^{266, 267}
 Immendorff, H., 155⁷, 357⁷, 361⁷, 461⁷
 Imoto, M., 143^{268, 269}, 144^{268, 269}, 145²⁶⁸, 349^{268, 269},
 465^{268, 269}
 Ingraham, J. N., 155⁴¹², 468⁴¹²
 Institute for Brown Coal and Mineral Oil Research,
 423
 Institution of Automotive Engineers, Australia, 20
 Interallied Conference of Pure and Applied Chem-
 istry, 5
 Ionescu, C. N., 26⁴⁰², 468⁴⁰²
 Ipatieff, V. N., 26^{277, 278}, 28²⁷⁶, 29^{274, 276, 282, 284}, 31²⁷⁶,
 33²⁷⁶, 40²⁸³, 44¹²⁵, 53²⁸⁵, 55²⁸⁵, 56²⁸⁵, 58²⁸⁵,
 60^{286, 287, 442}, 62²⁷¹, 63^{286, 287}, 94^{280, 281}, 95²⁷⁹,
 96^{270, 273, 279, 287, 288}, 97²⁷⁹, 98^{440, 441}, 99²⁷⁵, 100²⁸⁰,
 101⁴⁴¹, 108²⁸⁹, 129^{275a}, 140²⁷², 154²⁸⁰, 219²⁸³,
 221^{276, 284}, 235²⁷⁶, 245²⁸⁵, 247²⁸⁵, 257²⁷¹, 259²⁷¹,
 291^{270, 273, 279}, 293^{279, 441}, 295^{275, 440}, 299⁴⁴¹, 301²⁸⁰,
 305²⁸⁹, 323^{375a}, 333²⁷², 335²⁷², 463¹²⁵, 465²⁷⁰⁻²⁷⁶,
 466²⁷⁷⁻²⁸⁹, 468⁴⁴⁰, 469^{441, 442}
 Irineu, D., 191⁵²⁹, 387⁵²⁹, 470⁵²⁹
 Isacescu, D. A., 26⁴⁰², 468⁴⁰²
 Ishidate, M., 119^{15a, 15b}, 461^{15a, 15b}
 Ivanov, A. I., 44³⁴², 467³⁴²

J

- Jacobsen, O., 156²⁹⁰, 361²⁹⁰, 466²⁹⁰
 Jacobson, H. F., 21^{473a}, 469^{473a}
 Jakubowicz, W., 147⁵³⁶, 148⁵³⁶, 353⁵³⁶, 470⁵³⁶
 Janot, M. M., 147⁴⁸⁹, 353⁴⁸⁹, 469⁴⁸⁹
 Jeffrey, G. H., 102¹²³, 301¹²³, 463¹²³
 Jonas, K. G., 132⁵³⁷, 325⁵³⁷, 470⁵³⁷

Jones, R. L., 114²⁹¹, 309²⁹¹, 466²⁹¹
 Joshel, L. M., 206¹⁸⁶, 395¹⁸⁶, 464¹⁸⁶
 Jozitsch, J., 70²⁹², 269²⁹², 466²⁹²

K

Kadzhinov, V. N., 113²⁹³, 114²⁹³, 309²⁹³, 466²⁹³
 Kafuku, K., 149²⁹⁴, 353²⁹⁴, 466²⁹⁴
 Kametaka, T., 106⁶⁵⁰, 303⁶⁵⁰, 472⁶⁵⁰
 Kamm, E. D., 79²⁴⁴, 281²⁴⁴, 465²⁴⁴
 Kaplan, E. P., 40³⁷⁴, 241³⁷⁴, 467³⁷⁴
 —, J. F., 44^{358c}, 359^{358c}, 467^{358c}, 359^{358c}
 Karelova, L. E., 164^{342a}, 191^{342a}, 369^{342a}, 387^{342a}, 467^{342a}
 Karrer, P., 80²⁹⁵, 134²⁹⁶, 297²⁹⁶, 327²⁹⁶, 297²⁹⁶, 466²⁹⁵⁻²⁹⁷
 Karzhev, V. I., 295^{297a}, 466^{297a}
 Kassel, L. S., 30²⁹⁸, 466²⁹⁸
 Kay, F. W., 192²⁹⁹, 387²⁹⁹, 466²⁹⁹
 Kelber, C., 167³⁰⁰, 375³⁰⁰, 466³⁰⁰
 Kemp, L. C., 454
 Kennedy, R. M., 31³⁷⁵, 467³⁷⁵
 Kenner, J., 155²⁸, 158²⁷, 159²⁷, 357²⁸, 359²⁸, 365²⁷, 461^{27, 28}
 Kerr, C. A., 146⁴⁶⁹, 148⁴⁶⁹, 353⁴⁶⁹, 469⁴⁶⁹
 Kharasch, M. S., 61³⁰¹, 302³⁰², 166³⁰³, 167³⁰³, 253³⁰², 255³⁰¹, 371³⁰³, 373³⁰³, 375³⁰³, 466³⁰¹⁻³⁰³
 Kiess, M. A., 157⁵⁵⁹, 363⁵⁵⁹, 470⁵⁵⁹
 Kimball, G. E., 26^{303a}, 466^{303a}
 Kimberlin, Jr., C. N., 458
 Kimura, S., 44^{303b}, 466^{303b}
 Kiperash, M., 426
 Kiryushov, P. Y., 74³⁴³, 275³⁴³, 277³⁴³, 467³⁴³
 Kishner, N., 78³⁰⁴, 281³⁰⁴, 466³⁰⁴
 Kistiakowsky, G. B., 56³⁰⁵, 58^{304a}, 307³⁰⁷, 62^{140a}, 305³⁰⁵, 95¹⁰⁴, 164³⁰⁶, 165³⁰⁶, 245³⁰⁷, 291¹⁰⁴, 369³⁰⁶, 375³⁰⁶, 463¹⁰⁴, 140a⁴⁶⁶, 304a-307⁴⁶⁶
 Klages, A., 137³¹¹, 138³¹⁰, 311³¹¹, 161³⁰⁹, 162³⁰⁹, 163³⁰⁹, 213³¹⁰, 311³¹¹, 329³¹⁰, 311³¹¹, 367³⁰⁸, 309³⁰⁹, 369³⁰⁹, 399³¹⁰, 211⁴⁶⁶, 308-311⁴⁶⁶
 Klaphake, W., 450
 Klemm, A., 146¹³⁶, 353¹³⁶, 463¹³⁶
 Kloetzel, M. C., 201²⁶, 393²⁶, 461²⁶
 Knowlton, J. W., 32³¹², 477⁹⁵, 476⁴⁶⁶, 312⁴⁶⁹, 476⁴⁷⁷
 Kobilskaya, M. V., 28³⁷⁹, 33³⁷⁹, 37³⁷⁹, 40³⁸⁰, 42³⁸⁰, 235³⁷⁹, 380³⁷⁹, 239³⁸⁰, 241³⁷⁹, 467³⁷⁹, 380³⁸⁰
 Koch, 141
 Koelsch, C. F., 169³¹⁶, 176^{316a}, 189³¹³, 314³¹⁴, 315³¹⁵, 316³¹⁶, 190^{316a}, 377³¹⁶, 381^{316a}, 387³¹³, 314³¹⁴, 315³¹⁵, 316^{316a}, 466^{313-316a}
 Koeppl, F., 21^{317a}, 466^{317a}
 Kohler, E. P., 173³¹⁷, 379³¹⁷, 466³¹⁷
 Kohlrausch, K. W. F., 21^{317a}, 466^{317a}
 Komarewsky, V. I., 8²⁶, 26²⁷⁸, 29²³², 42³¹⁸, 319³¹⁹, 94²⁸⁰, 281²⁸¹, 100²³⁰, 154²⁸⁰, 239³¹⁸, 243³¹⁹, 301²⁸⁰, 465²³², 466²⁷⁸, 280²⁸⁰, 281²⁸¹, 318³¹⁸, 319³¹⁹
 Komppa, G., 117^{320a}, 119^{319a}, 121³²⁰, 311^{320a}, 317³²⁰, 466^{319a, 320, 320a}
 Kon, G. A. R., 151^{65a}, 202³²¹, 204³²¹, 355^{65a}, 393³²¹, 430⁴⁶², 462^{65a}, 466³²¹
 —, S. K., 133²¹¹, 325²¹¹, 327²¹¹, 464²¹¹
 Kondakov, S.-L., 119³²², 143³²², 144³²², 315³²², 349³²², 351³²², 466³²²
 Konovalov, M., 407
 Kootz, H., 169⁵⁶⁹, 377⁵⁶⁹, 471⁵⁶⁹
 Köppl (see Koeppl)
 Korolev, S., 72¹⁸², 271¹⁸², 464¹⁸²
 Kosack, H., 177⁶⁵⁴, 381⁶⁵⁴, 472⁶⁵⁴
 Koshelev, A. F., 98⁵⁹⁶, 295⁵⁹⁶, 471⁵⁹⁶
 Krafft, F., 86³²³, 287³²³, 466³²³
 Krechkov, A. P., 154³⁷⁶, 357³⁷⁶, 467³⁷⁶
 Kronstein, A., 415⁴⁶⁶, 466^{323a}
 Kuhn, R., 167³²⁴, 466³²⁴
 Kutscherov, L. M., 71³²⁶, 73³²⁵, 271³²⁶, 466³²⁵, 326³²⁶
 Kuwata, T., 143³²⁷, 144^{327a}, 337³²⁷, 327a^{327a}, 466³²⁷, 327a^{327a}

L

Lafont, J., 143⁷⁵, 76⁷⁶, 144⁷⁴, 75⁷⁵, 76⁷⁶, 77³²⁸, 345³²⁸, 347^{74, 75}, 347³²⁸, 349⁷⁶, 462⁷⁴⁻⁷⁷, 466³²⁸
 Lagermark, H., 71¹⁶⁴, 464¹⁶⁴
 Laidler, K. J., 26^{216a}, 464^{216a}
 Lamb, G. G., 453⁴⁵⁴
 Lambert, P., 21^{3a}, 461^{3a}
 Langedijk, S. L., 21^{643a}, 102⁶⁴⁴, 299^{643a}, 472^{643a}, 644⁶⁴⁴
 Langmuir, 18
 Laughlin, K. C., 65³²⁹, 66³²⁹, 261³²⁹, 263³²⁹, 466³²⁹

Lawrence, C. A., 44¹²¹, 204¹²¹, 205¹²¹, 210¹²², 393¹²¹, 395¹²¹, 397¹²², 463^{121, 122}
 Lawroski, S., 64⁶⁴², 472⁶⁴²
 Lebedev, B. M., 170^{43a}, 377^{43a}, 461^{43a}
 Lebedev, S. V., 71³³⁰, 74³³¹, 333³³³, 76³³³, 170³³², 188³³², 269³³⁰, 275³³¹, 277³³³, 279³³³, 377³³², 387³³², 466³³⁰⁻³³³
 Lecomte, J., 21^{3a}, 461^{3a}
 Leendertse, J. J., 122⁶³⁷, 317⁶³⁷, 472⁶³⁷
 Legutke, G., 119^{258a}, 127^{258a}, 321^{258a}, 465^{258a}
 Lemmel, L., 190⁵⁷⁴, 387⁵⁷⁴, 471⁵⁷⁴
 Lepin, A. I., 159³³⁴, 335³³⁵, 365³³⁴, 335³³⁵, 466³³⁴, 335³³⁵
 LeRosen, A. L., 428
 Lespieau, R., 86³³⁶, 287³³⁶, 467³³⁶
 Levina, R. Y., 44^{336a}, 340³⁴⁰, 341³⁴¹, 342³⁴², 344³⁴⁴, 346³⁴⁶, 347³⁴⁷, 348³⁴⁸, 669a^{669a}, 69⁶⁷⁰, 74³³⁷, 338³³⁸, 343³⁴³, 76³³⁸, 106³⁴⁹, 121⁶⁶⁹, 134³⁴⁴, 141^{669a}, 161³³⁸, 339³³⁹, 345^{346a}, 348³⁴⁸, 163^{346a}, 164³³⁸, 342a^{342a}, 345³⁴⁵, 180^{344a}, 191^{342a}, 265⁶⁷⁰, 275³³⁷, 338³³⁸, 343³⁴³, 277³⁴³, 279³³⁸, 303³⁴⁹, 317⁶⁶⁹, 327³⁴⁴, 345^{669a}, 367³³⁸, 339³³⁹, 345^{346a}, 348³⁴⁸, 369³³⁸, 369^{342a}, 345³⁴⁵, 383^{344a}, 387^{342a}, 467^{336a-349}, 472⁶⁶⁹, 669a^{669a}, 472⁶⁷⁰
 —, S. Y., 44³⁴⁴, 134³⁴⁴, 327³⁴⁴, 467³⁴⁴
 Levshuk, M. Y., 143^{349a}, 337^{349a}, 467^{349a}
 Levy, 96
 Lewis, 18
 Lewis, G. N., 57³⁵⁰, 165^{350a}, 369^{350a}, 375^{350a}, 467³⁵⁰, 350a^{350a}
 Lichtenstadt, L., 191⁵²⁹, 387⁵²⁹, 470⁵²⁹
 Linstead, R. P., 44^{95b}, 350b^{95b}, c^{95b}, 113³⁷, 114²⁵², 291²⁹¹, 115³⁵¹, 123³⁵², 127¹⁷⁰, 131²⁵², 353³⁵³, 145³⁵³, 197^{95a}, 309³⁷, 252²⁹¹, 351³⁵¹, 323¹⁷⁰, 353³⁵³, 325²⁵³, 351³⁵³, 389^{95a}, 391^{95a}, 461³⁷, 462^{95a}, 95b^{95b}, 464¹⁷⁰, 465²⁵², 253²⁵³, 466²⁹¹, 467^{350b-353}
 Lipkin, D., 165^{350a}, 369^{350a}, 375^{350a}, 467^{350a}
 Lipp, M., 91^{353a}, 119^{353b}, 467^{353a, b}
 —, P., 113³⁵⁴, 119^{355a, b}, 122³⁵⁵, 317³⁵⁵, 467^{354-355b}
 Livschitz, S. E., 23³⁸¹, 28³⁷⁹, 33³⁷⁹, 37³⁷⁹, 40³⁸⁰, 42³⁸⁰, 235³⁷⁹, 380³⁸⁰, 239³⁸⁰, 241³⁷⁹, 407⁴⁰⁷, 408^{380a}, 467³⁷⁹⁻³⁸¹
 Loesche, A., 146¹³⁶, 353¹³⁶, 463¹³⁶
 Lorang, H. F. J., 58⁴²⁰, 59^{609a}, 249⁴²⁰, 251^{609a}, 445⁴⁴⁵, 468⁴²⁰, 471^{609a}
 Lorentz, H. A., 21^{355c}, 467^{355c}
 Lorenz, L., 21^{355d}, 467^{355d}
 Loschkomoinikov, A. I., 106³⁴⁹, 303³⁴⁹, 467³⁴⁹
 Lovell, W. G., 31²¹⁶, 98²¹⁶, 100²¹⁵, 101²¹⁵, 229²¹⁶, 231²¹⁶, 293²¹⁵, 299²¹⁵, 464²¹⁵, 216²¹⁶
 Lucas, H. J., 61^{356, 357}, 467^{356, 357}
 Lutgerhorst, A. G., 119^{71a}, 462^{71a}
 Luttringer, A., 84^{141a}, 285^{141a}, 463^{141a}
 Lux, A. R., 156⁵⁶⁰, 470⁵⁶⁰
 Lynch, C. S., 32^{357a}, 231^{357a}, 467^{357a}
 Lyubomilov, V. I., 143^{349a}, 337^{349a}, 467^{349a}

M

Magel, T. T., 165^{350a}, 369^{350a}, 375^{350a}, 467^{350a}
 Maitland, P., 174³⁵⁸, 379³⁵⁸, 467³⁵⁸
 Makaeva, Z., 98⁵⁹⁷, 102⁵⁹⁷, 295⁵⁹⁷, 301⁵⁹⁷, 471⁵⁹⁷
 Mallison, H., 110⁶²¹, 305⁶³¹, 472⁶³¹
 Mansfield, J., 94⁵²³, 470⁵²³
 —, J. V., 166³⁰³, 167³⁰³, 371³⁰³, 373³⁰³, 375³⁰³, 466³⁰³
 Manz, G., 186⁸⁸, 385⁸⁸, 462⁸⁸
 Marcus, E., 159⁵¹⁹, 365⁵¹⁹, 470⁵¹⁹
 Marder, M., 21^{358a}, 407^{500a}, 420⁴²⁰, 421^{358a}, 467^{358a}, 469^{500a}
 Margolis, E. I., 105⁶⁷¹, 303⁶⁷¹, 472⁶⁷¹
 Markovnikov, 407
 Marks, E. M., 451
 Martin, R. H., 432
 Marvel, C. S., 44^{358b}, c³⁵⁹, 361³⁶¹, 81¹³², 499⁴⁹⁹, 563⁵⁶³, 86⁴⁹⁹, 563⁵⁶³, 87¹³², 499⁴⁹⁹, 575⁵⁷⁵, 88⁵⁶⁴, 179³, 175¹⁷⁵, 217²¹⁷, 240²⁴⁰, 360³⁶⁰, 182²⁴⁰, 393³⁹³, 564⁵⁶⁴, 183¹⁹², 217²¹⁷, 240²⁴⁰, 360³⁶⁰, 562⁵⁶², 184³, 175¹⁷⁵, 564⁵⁶⁴, 592⁵⁹², 185²⁴², 200⁴⁷⁴, 287⁴⁹⁹, 289¹³², 499⁴⁹⁹, 575⁵⁷⁵, 381³, 175¹⁷⁵, 383²⁴⁰, 392³⁹², 564⁵⁶⁴, 385²⁴², 385⁵⁶⁴, 592⁵⁹², 391⁴⁷⁴, 429⁴²⁹, 461³, 463¹³², 464¹⁷⁵, 192¹⁹², 465²¹⁷, 240²⁴⁰, 242²⁴², 467^{358b-361}, 468³⁹³, 469⁴⁷⁴, 499⁴⁹⁹, 470⁵⁶²⁻⁵⁶⁴, 471⁵⁷⁵, 592⁵⁹²
 Masumoto, B., 197¹⁴³, 391¹⁴³, 463¹⁴³
 Matignon, C., 56³⁶², 467³⁶²
 Matsui, M., 181⁸⁶, 383⁸⁶, 462⁸⁶
 Matsuno, K., 148³⁶³, 149³⁶³, 364³⁶⁴, 467³⁶³, 364³⁶⁴
 Mattox, W. J., 8
 Matuschkina, A., 170³³², 188³³², 377³³², 387³³², 466³³²

Mavity, J. W., 8, 29 232, 465 232
 Mayer, F., 191 365, 192 365, 387 365, 467 365
 Mayneord, W. V., 205 113, 207 119, 209 119, 210 119,
 211 113, 395 113, 397 113, 463 113, 119
 Mayo, F. R., 166 303, 167 303, 371 303, 373 303, 375 303,
 466 303
 McAteer, J. H., 30 366, 384, 385, 31 366, 384, 32 385, 33 366, 385,
 34 366, 41 366, 49 384, 385, 219 366, 384, 385, 227 366,
 229 384, 385, 233 385, 235 366, 385, 237 366, 467 366, 384,
 468 385
 McDowall, F. H., 149 367, 355 367, 467 367
 McKee, R. H., 28 368, 467 368
 McMillan, F., 31 135a, 49 135a, 225 135a, 463 135a
 McVey, W. C., 211 141, 212 141, 397 141, 463 141
 Meerwein, H., 119 369, 370, 122 369, 143 369, 370, 317 369,
 450, 467 369, 370
 Meinert, R. N., 81 370a, 285 370a, 467 370a
 Mereshkovski, B. K., 73 371, 108 372, 125 373, 271 371
 273 371, 305 372, 319 373, 467 371-373
 Meister, M., 165 447, 371 447, 469 447
 Merkel, E., 164 645, 472 645
 Meshcheryakov, A. P., 36 437, 40 374, 437, 41 437, 42 437,
 55 437, 64 437, 237 437, 239 427, 241 374, 437, 261 437,
 467 374, 468 437
 Messerly, G. H., 31 375, 467 375
 Meunier, P. L., 66 643, 472 643
 Meyer, J., 124 490, 131 490, 325 490, 469 490
 —, K., 146 137, 353 137, 463 137
 —, V., 408 375a, 467 375a
 Michaelis, K. O. A., 44 350b, 467 350b
 Mikchailenko, Y. Y., 154 376, 357 376, 467 376
 Millidge, A. F., 44 350c, 325 253, 465 253, 467 350c
 Mills, W. H., 174 358, 379 358, 467 358
 Mingazzini, M., 124 490, 131 490, 325 490, 469 490
 Mizusima, S., 428
 Mochida, T., 140 377, 143 377, 333 377, 467 377
 Moerbeck, B. H., 37 561a, 38 561a, 69 561a, 265 561a,
 470 561a
 Mohr, E., 101 378, 467 378
 Moldavsky, B. L., 23 381, 28 379, 30 382, 31 382, 32 382a,
 33 379, 37 379, 40 380, 42 380, 49 382, 221 382, 227 382,
 229 382, 231 382a, 233 382a, 235 379, 380, 382a, 239 380,
 241 379, 407, 408 380a, 467 379-382a
 Montaland, L., 143 383, 333 383, 335 383, 467 383
 Montañés, J. M., 333 201a, 464 201a
 Montgomery, C. W., 30 384, 385, 31 384, 32 385, 33 385,
 49 384, 385, 219 384, 385, 229 384, 385, 233 385, 467 384,
 468 385
 Moore, G. E., 101 386, 468 386
 Morino, Y., 428
 Morrell, J. C., 21 58a, 59 153, 581b, 60 158, 68 158, 69 158,
 247 158, 253 158, 265 158, 267 158, 433, 462 58a, 463 158,
 471 581b
 Morton, A., 192 299, 387 299, 466 299
 Moureu, C., 182 389, 183 389, 197 387, 388, 391 387, 388,
 468 387-389
 —, H., 56 362, 467 362
 Moyse, H. W., 61 356, 467 356
 Mueller, C., 159 646, 365 646, 472 646
 —, F., 408, 467 375a
 —, K., 135 22, 329 22, 461 22
 —, M. B., 44 359, 361, 467 359, 361
 —, Cunradi, M., 55 266, 267, 56 266, 267, 245 266-267,
 465 266, 267
 Mulcey, P. A., 140 391, 142 390, 333 391, 468 390, 391
 Müller (see Mueller)
 Mumford, S. A., 21 391a, 468 391a
 Mundici, C. M., 155 392, 361 392, 468 392
 Munro, H. E., 182 393, 383 393, 468 393
 Murayama, Y., 128 394, 323 394, 347 394, 468 394
 Murray, A. R., 165 578, 167 324, 578, 371 578, 375 578,
 466 324, 471 578
 Muskat, I. E., 175 395, 381 395, 468 395

N

Naber, A. D., 201 134a, 393 134a, 463 134a
 Nametkin, S., 407, 468 395a
 Narracott, E. S., 202 321, 204 321, 393 321, 466 321
 Nash, A. W., 95 224, 465 224
 —, C. W., 65 329, 66 329, 261 329, 263 329, 466 329
 Naves, Y. R., 115 395b, 429, 468 395b
 Nef, J. U., 93 396, 468 396
 Nefontova, S., 407, 468 395a
 Nemtsov, M. S., 68 397, 263 397, 468 397

Nenitzescu, C. D., 26 402, 33 401, 35 401, 94 398, 98 399,
 100 399, 102 400, 235 401, 237 401, 293 399, 299 399,
 301 400, 468 398-402
 Neunhoeffer, O., 119 257c, 465 257c
 Newmann, F. H., 199 403, 391 403, 468 403
 Newport Industries, Inc., 44 428b, 468 428b
 Nightingale, D., 157 404, 405, 158 405, 405a, 363 404, 405, 405a,
 365 405a, 431, 468 404-405a
 Nikolaev, A. A., 94 406, 468 406
 Nikolaeva, A. F., 41 407, 408, 101 454, 102 455, 126 408a,
 235 403, 239 407, 297 454, 301 455, 468 407-408a, 469 454, 455
 Nishida, K., 150 409, 410, 355 409, 468 409, 410
 Nisovkina, T. V., 30 382, 31 382, 32 382a, 49 392, 68 397,
 221 382, 227 382, 229 382, 231 382a, 233 382a, 235 382a,
 263 397, 467 382, 382a, 468 397
 Norris, J. F., 26 411, 61 413, 62 413, 63 413, 155 412, 414,
 155 415, 416, 257 413, 357 414, 415, 359 415, 361 414, 415,
 468 411-416
 Nozoe, T., 149 294, 353 294, 466 294
 N. P. N. News Bureau, 433
 N. V. de Bataafsche Petroleum Maatschappij,
 29 418, 420d, 422, 30 419, 422, 32 420a, 58 420, 421, 59 417,
 69 417a, 421a, 219 416a, 418, 419, 422, 423, 221 416b, 223 420b, c,
 227 418, 231 420a, 233 420a, 249 417, 417a, 420, 421a, 251 421,
 257 421a, 265 417a, 421a, 439, 441-449, 468 416a-423
 Nyman, G. A., 117 320a, 121 320, 311 320a, 317 320,
 466 320, 320a

O

Oberfell, G. G., 26 424, 468 424
 Oblad, A. G., 456
 Ocon, E. A., 451, 452
 Ogg, Jr., R. A., 66 425, 96 426, 291 426, 468 425, 426
 Oliviero, 144 78, 345 78, 347 78, 462 78
 Opel, E., 72 182, 271 182, 464 182
 Orcutt, R. M., 204 427, 393 427, 468 427
 Orechov, A. P., 186 428, 385 428, 468 428
 Orlov, N., 29 282, 466 282
 Otto, B., 61 301, 545, 255 301, 545, 466 301, 470 545
 —, R., 165 428a, 369 428a, 468 428a
 Overhoff, J., 21 643a, 299 643a, 472 643a
 Owens, W. M., 79 244, 281 244, 465 244

P

Palkin, S., 117 217b, 142 217a, 311 217b, 331 217a, 429,
 465 217a, b
 Palmer, R. C., 44 428b, 468 428b
 Panov, E. M., 180 344a, 383 344a, 467 344a
 Parks, G. S., 21 428c, 59 586a, 101 396, 426, 468 396, 428c,
 471 586a
 Parrish, C. I., 21 159, 463 159
 Parsons, C. L., 5
 Pauling, L., 26 429-433, 428, 468 429-433
 —, L. C., 6
 Pavlenko, A. V., 193 453, 389 453, 469 453
 Pavlov, G. S., 44 671a, b, 472 671a, b
 —, P. Y., 42 659, 239 659, 472 659
 Peignier, P., 119 609c, 471 609c
 Peppel, W. J., 81 563, 86 563, 179 360, 183 360, 467 360,
 470 563
 Perlman, D., 203 434, 393 434, 468 434
 Perrottet, E., 115 395b, 429, 468 395b
 Perry, D., 22 435, 468 435
 —, H. O., 158 561, 365 561, 470 561
 Pesin, L. M., 143 349a, 337 349a, 467 349a
 Petrov, A., 29 282, 466 282
 —, A. D., 23 436, 36 437, 40 437, 41 437, 42 437, 55 437,
 64 437, 65 436, 438, 68 436, 237 437, 239 437, 241 437,
 261 436, 437, 438, 265 436, 468 436-438
 —, D. A., 161 345, 164 345, 367 345, 369 345, 467 345
 Petrovici, O., 118 21, 315 21, 461 21
 Peuffaillit, L., 143 439, 349 439, 468 439
 Peyer, E., 185 491, 385 491, 469 491
 Pfeiffer, M., 107 485, 469 485
 Phillips, J. W. C., 21 391a, 468 391a
 —, N. E., 31 216, 229 216, 231 216, 464 216
 Pickett, L. W., 61 301, 545, 255 301, 545, 466 301, 470 545
 Picoux, R., 142 148, 333 148, 463 148
 Pier, M., 452
 Pim, F. B., 41 65c, 462 65c
 Pines, H., 8, 26 273, 29 284, 40 232a, 283, 53 285, 55 285,
 56 285, 58 285, 60 286, 287, 442, 63 286, 287, 96 287, 98 440, 441,
 101 441, 299 441, 465 232a, 466 278, 283-287, 468 440,
 469 441, 442

Pitzer, K., 21 442a, 469 442a
 —, K. S., 21 477b, 43 477b, 44 477b, 49 477b, 427, 469 477b
 Planckh, R., 407 574d, 471 574d
 Plotnikova, A. F., 143 349a, 337 349a, 467 349a
 Podbielniak Centrifugal Super-Contractor Co.
 21 442b, 469 442b
 Poeckel, I., 66 38, 119 39, 461 38, 39
 Pollakova, O. I., 98 598, 295 598, 471 598
 Popkin, A. H., 64 642, 472 642
 Porter, C. W., 27 443, 444, 469 443, 444
 Potapova, A. A., 44 346, 467 346
 Power Patents Co., 453
 Pressman, D., 55 658, 472 658
 Prevost, C., 74 445, 277 445, 469 445
 Price, C. C., 102 446, 165 447, 371 447, 469 446, 447
 Priest, W. J., 96 426, 291 426, 468 426
 Prins, H. J., 141 448, 343 448, 469 448
 Prokopetz, E. I., 98 452, 101 452, 114 449, 122 451,
 123 451, 193 450, 453, 293 452, 297 452, 309 449, 317 451,
 389 450, 453, 469 449-453
 Prosen, E. J. R., 21 477b, 35 453a, 477a, 43 477b, 44 477b,
 427, 469 453a, 477a, b
 Puchkov, P. V., 41 407, 408, 101 453b, 454, 102 455, 126 408a,
 235 408, 239 407, 297 453b, 454, 301 453b, 455, 468 407-408a,
 469 453b-455

Q

Quiggle, D., 64 642, 472 642

R

Ramart-Lucas, P., 161 456, 457, 164 456, 170 453, 367 456,
 367 457, 369 456, 376, 377 458, 469 456-458
 Raney, 388
 Rao, B. S., 138 101, 459, 329 459, 462 101, 469 459
 Raoult, 32
 Raper, R., 174 106, 379 106, 463 106
 Rathmann, F. H., 96 472, 291 472, 469 472
 Read, J., 128 103, 135 103, 140 103, 323 103, 329 103,
 343 103, 463 103
 Rebner, J., 117 459a, 143 459a, 311 459a, 337 459a, 469 459a
 Reich, V. N., 159 335, 365 335, 466 335
 Reinhold Publishing Corporation, 5
 Reisman, J., 140 133a, 143 133a, 460, 144 460, 345 460,
 347 133a, 349 133a, 463 133a, 469 460
 Rentschler, M., 110 628, 305 628, 472 628
 Reuter, L., 86 323, 287 323, 466 323
 —, R., 61 413, 62 413, 63 413, 257 413, 468 413
 Riban, J., 140 462, 141 461, 462, 463, 464, 143 462, 464, 331 462,
 343 462, 464, 469 461-464
 Rice, O. K., 95 465, 469 465
 Richter, F., 44 467, 118 466, 140 466, 311 466, 469 466, 467
 Ridi, M. S. El, 133 210, 211, 325 210, 211, 327 210, 211,
 464 210, 211
 Rieger, W. H., 44 361, 467 361
 Riesz, C. H., 42 319, 243 319, 466 319
 Risi, J., 169 468, 377 468, 469 468
 Robertson, A., 147 246, 353 246, 465 246
 —, J. M., 146 469, 148 469, 353 469, 469 469
 Robinson, A. M., 203 120, 206 115, 123, 210 124, 393 120,
 395 115, 123, 397 124, 463 115, 120, 123, 124
 —, R., 148 470, 469 470
 Roblin, Jr., R. O., 162 73, 163 73, 471, 367 73, 471, 369 73,
 369 471, 462 73, 469 471
 Robson, A. C., 174 106, 379 106, 463 106
 Roe, E., 205 113, 207 119, 209 119, 210 119, 211 113,
 395 113, 119, 397 113, 119, 463 113, 119
 Roginski, S. Z., 96 472, 291 472, 469 472
 Rogowski, W., 55 166, 245 166, 464 166
 Rose, A., 64 473, 469 473
 Rosenbaum, E. J., 21 473a, 469 473a
 Rosenwald, R. H., 169 316, 189 316, 377 316, 387 316,
 466 316
 Rossander, S. S., 200 474, 391 474, 469 474
 Rossini, F. D., 21 475a, 477b, 31 475, 32 312, 477, 33 475,
 35 453a, 477a, 43 477b, 44 477b, 95 476, 427, 466 312,
 469 453a, 475-477b
 Roux, L., 190 478, 469 478
 Rozanov, N. A., 97 479, 480, 293 479, 480, 469 479, 480
 Rubinstein, D., 155 414, 357 414, 361 414, 468 414
 Rudakov, G. A., 44 480a, 128 480a, 143 536, 323 480a,
 333 536, 335 536, 337 536, 469 480a, 471 536
 Rudkovsky, D. M., 58 199, 200, 59 199, 249 199, 200,
 251 200, 253 199, 200, 257 200, 267 200, 450, 464 199, 200
 Ruhoff, J. R., 56 305, 58 304a, 62 305, 466 304a, 305

Runge, F., 55 266, 267, 56 266, 267, 245 266, 267, 465 266, 267
 Rupe, H., 213 481, 399 481, 469 481
 Rutovski, B. N., 143 349a, 337 349a, 467 349a
 Ruzicka, L., 78 486, 79 482, 486, 107 485, 124 490, 131 484,
 131 490, 494, 495, 132 494, 146 483, 488, 147 487, 489, 493,
 185 491, 281 482, 486, 325 484, 490, 494, 495, 353 488, 489, 492,
 353 493, 385 491, 469 482-495
 Ryan, J. D., 170 522, 188 522, 377 522, 470 522

S

Sabatier, P., 142 496, 469 496
 Sachanan, A. N., 60 497, 64 497, 469 497
 Sachse, H., 101 498, 469 498
 Sakara, N., 72 182, 271 182, 464 182
 Salmon-Legagneur, E., 170 458, 377 458, 469 458
 Salzberg, P. L., 81 499, 86 499, 87 499, 287 499, 289 499,
 469 499
 Sano, T., 119 15b, 461 15b
 Saprikin, F. Y., 155 139, 357 139, 359 139, 463 139
 Sauermilch, W., 174 679, 175 679, 379 679, 473 679
 Schaad, R. E., 53 285, 55 285, 56 285, 245 285, 247 285,
 466 285
 Schaarschmidt, A., 23, 407 500, 500a, 408, 413, 419,
 469 500, 500a
 Schering - Kahlbaum A. - G., 117 459a, 502, 503, 504,
 118 504a, 508, 508a, 509, 510, 511, 511a, 512a, 513, 514, 126 501, 521,
 140 502, 143 502-505, 503, 509-512, 513, 514, 601a, 311 459a, 503, 505,
 311 506, 509, 510, 513, 313 502, 504, 508, 511, 514, 319 501, 507,
 321 521, 337 459a, 503, 513, 339 502, 503, 504, 505, 508, 509, 510,
 339 513, 514, 601a, 341 502, 511, 512, 514, 601a, 440, 441, 449,
 450, 469 459a, 501-503, 470 504-514, 521, 471 601a
 Scheunert, A., 76 632, 279 632, 472 632
 Schiffner, R., 191 365, 192 365, 387 365, 467 365
 Schiller, H. von, 145 538, 351 538, 470 538
 Schimmel and Co., 76 515, 279 515, 470 515
 Schinz, H., 107 485, 469 485
 Schlenk, W., 159 519, 165 516, 167 517, 168 516, 517, 518,
 365 519, 369 516, 375 517, 377 516, 518, 470 516-519
 Schmerling, L., 8, 60 286, 287, 442, 63 286, 287, 96 287,
 466 286, 287, 469 442
 Schmidt, P., 84 653, 285 653, 472 653
 Schneider, H. G. R., 33 520, 470 520
 Schoeller, W., 126 521, 321 521, 470 521
 Schoenemann, K., 452
 Schoepfle, C. S., 170 522, 188 522, 377 522, 470 522
 Scholl, R., 94 523, 524, 192 525, 526, 389 525, 526, 470 523-526
 Schrauth, W., 106 527, 470 527
 Schreiber, W., 171 57, 176 57, 379 57, 381 57, 462 57
 Schroeter, G., 191 529, 194 528, 196 528, 387 529, 389 528,
 470 528, 529
 Schuit, G. C. A., 31 135a, 529a, 32 529a, 33 529a, 34 529a,
 49 135a, 529a, 59 529a, 63 529a, 65 529a, 98 529a, 100 529a,
 102 529a, 103 529a, 126 529a, 225 135a, 529a, 227 529a,
 233 529a, 235 529a, 237 529a, 249 529a, 259 529a, 261 529a,
 293 529a, 299 529a, 301 529a, 303 529a, 319 529a, 439,
 457, 463 135a, 470 529a
 Schwarz, A., 167 300, 375 300, 466 300
 Schwenk, E., 126 521, 321 521, 470 521
 Scott, N. D., 190 530, 387 530, 470 530
 Sdzitowiecky, W., 96 288, 466 288
 Seer, C., 94 523, 524, 192 525, 389 525, 470 523-525
 Seligman, A. M., 206 186, 395 186, 464 186
 Semmler, F. W., 76 531, 532, 533, 78 539, 115 533, 534,
 131 535, 132 537, 143 534, 145 538, 147 536, 148 536,
 279 531, 532, 533, 281 539, 311 533, 325 535, 537, 351 533,
 353 536, 470 531-539, 471 533
 Serebriakova, E. K., 58 199, 200, 59 199, 540, 249 199, 200,
 251 200, 540, 253 199, 200, 540, 257 200, 267 200, 450,
 464 199, 200, 470 540
 Sergienko, S. R., 44 540a, 540b, 470 540a, 540b
 Sever'yanova, M. G., 295 297a, 466 297a
 Shcheglova, N. A., 161 346a, 163 346a, 367 346a, 467 346a
 Shchukin, V., 65 438, 261 438, 468 438
 Sheffield, D. H., 141 541, 542, 343 542, 470 541, 542
 Shell Development Co., 26 5c, 29 165a, 31 135a, 49 135a,
 60 257a, 65 257a, 69 257a, 221 165a, 223 165a, 225 135a, 165a,
 249 257a, 253 257, 257 257a, 261 257a, 265 257a, 267 257,
 445, 446, 451, 455, 457, 458, 461 5c, 463 135a,
 464 165a, 465 257, 257a
 Shell Oil Co., Inc., 432
 Sherman, J., 26 431, 432, 543, 468 431, 432, 470 543
 Sherrill, M. L., 61 301, 544, 545, 255 301, 545, 257 544,
 466 301, 470 544, 545
 Shibaev, A., 72 182, 271 182, 464 182
 Shiffler, W. H., 452

Shterner, R. A., 32 382a, 231 382a, 233 382a, 235 382a, 467 382a
 Shuikin, N. I., 112 671c, 307 671c, 472 671c
 Sidel'kovskaya, F. P., 103 598ab, 106 598aa, 303 598aa, 303 598ab, 471 598aa, 598ab
 Siebert, C., 173 613, 379 613, 472 613
 Silchenko, E. I., 114 545a, 309 545a, 470 545a
 Sillevs, K. H. A., 44 71, 462 71
 Simamura, O., 166 607, 608, 167 607, 609, 371 607, 608, 373 607, 608, 471 607-609
 Simonsen, J. L., 138 101, 459, 139 546, 329 459, 331 546, 462 101, 469 459, 470 546
 Simpson, T. P., 61 357, 467 357
 Siverstev, A. P., 28 546a, 35 546a, 39 546a, 237 546a, 239 546a, 241 546a, 470 546a
 Sivova, A. N., 295 297a, 466 297a
 Skraup, S., 99 547, 297 547, 470 547
 Slobodin, Y. M., 70 549, 552, 71 548, 72 551, 553, 74 333, 75 551, 553, 76 333, 82 552, 84 548, 554, 128 550, 175 555, 181 555, 269 549, 552, 271 548, 551, 553, 273 551, 277 333, 551, 277 553, 279 333, 285 552, 554, 287 548, 323 550, 379 555, 383 555, 466 333, 470 548-555
 Slooff, G., 119 71a, 462 71a
 Slovokhotova, T. A., 98 593a, 295 593a, 471 593a
 Smakula, A., 165 556, 375 556, 470 556
 Smelser, H. W., 158 405a, 363 405a, 365 405a, 468 405a
 Smirnov, K. M., 44 341, 467 341
 Smith, D. F., 140 557, 331 557, 470 557
 —, H. A., 56 305, 58 304a, 62 305, 466 304a, 305
 —, H. G., 128 103, 135 103, 140 103, 323 103, 329 103, 343 103, 463 103
 —, L. I., 156 558, 560, 157 405, 559, 158 405, 558a, 561, 361 558, 363 405, 558, 559, 365 558a, 561, 468 405, 470 558-561
 —, W. R., 58 307, 164 306, 165 306, 245 307, 369 306, 375 306, 466 306, 307
 Smithuysen, W. C. B., 32 420a, 231 420a, 233 420a, 455, 468 420a
 Smittenberg, J., 21 643a, 37 561a, 38 561a, 69 561a, 102 644, 265 561a, 299 643a, 470 561a, 472 643a, 644
 Solmssen, U., 134 296, 297, 327 296, 297, 466 296, 297
 Sommer, F., 137 311, 138 311, 213 311, 329 311, 399 311, 466 311
 Soskina, E. A., 68 397, 263 397, 468 397
 Sparks, W. J., 81 563, 86 563, 183 562, 470 562, 563
 Spornitz, K. E., 78 539, 281 539, 470 539
 Stampfli, J. G., 88 564, 182 564, 184 564, 383 564, 470 564
 Standard Oil Co. (Indiana), 432, 433, 452-454, 456-458
 Standard Oil Co. of California, 452
 Standard Oil Development Co., 26 5c, 32 37a, 357a, 229 37a, 231 37a, 357a, 441, 444, 445, 448, 458, 461 5c, 37a, 467 357a
 Stavely, H. E., 150 565, 355 565, 471 565
 Stewart, T. D., 415 565a, 471 565a
 Stobbe, H., 180 566, 381 566, 471 566
 Stoermer, R., 164 567, 165 567, 167 567, 570, 169 569, 199 568, 369 567, 570, 371 567, 375 567, 570, 377 569, 391 568, 471 567-570
 Stoffel, F., 165 423a, 369 423a, 468 423a
 Stoll, M., 107 485, 131 494, 132 494, 147 492, 493, 325 494, 353 492, 493, 469 485, 492-494
 Stratford, R., 40 228, 571, 102 571, 103 228, 571, 301 571, 303 571, 363 571, 465 228, 471 571
 Straus, F., 165 572, 167 572, 175 572, 177 572, 190 573, 574, 369 572, 371 572, 375 572, 381 572, 387 573, 574, 471 572-574
 Stscherbak, B. A., 108 672, 305 672, 472 672
 Stuecklen, H., 56 99, 462 99
 Suau, E., 140 133a, 143 133a, 347 133a, 349 133a, 463 133a
 Subramanian, K. S., 138 101, 462 101
 Sugden, S., 21 574c, 420 574c, 421 574a-c, 422, 423, 471 574a-c
 Suida, H., 407 574d, 471 574d
 Sweet, R. S., 87 575, 289 575, 471 575
 Swientoslawski, W., 21 575a, 471 575a
 Syrkin, J., 26 575aa, 190 575aa, 471 575aa
 Szayna, A., 28 368, 68 259, 263 259, 465 259, 467 368
 Szebellédy, L., 408 575b, 409, 471 575b

T

Tait, T., 41 65c, 462 65c
 Takano, T., 140 254, 255, 141 255, 143 255, 256, 341 255, 256, 343 254, 255, 465 254-256
 Tanatar, S., 95 576, 577, 96 577, 291 576, 577, 471 576, 577
 Tappe, W., 119 253a, 126 253, 127 253a, 321 253, 2 8a, 465 253, 253a

Tarasova, G. A., 98 593b, 295 593b, 471 593b
 Taubadel, H., 172 61, 379 61, 461 61
 Taylor, H. S., 27 219, 220, 44 218, 221, 64 220, 66 220, 67 220, 259 220, 261 220, 263 220, 465 218-221
 —, R. G., 158 405a, 363 405a, 365 405a, 468 405a
 —, T. W. J., 165 578, 167 324, 578, 371 578, 375 578, 466 324, 471 578
 Tcheoufaki, 177 229, 381 229, 465 229
 Teeple, J. E., 5
 Temkin, M., 26 578a, 471 578a
 Texaco Development Corp., 442, 448, 450
 Texas Co., The, 26 5c, 454, 456, 461 5c
 Thiele, J., 187 579, 189 580, 385 579, 387 580, 471 579, 580
 Thomas, C. L., 8, 59 158, 581b, 60 158, 581a, 68 158, 69 158, 581a, 89 581, 247 158, 253 158, 581a, 265 158, 581a, 267 158, 452, 463 158, 471 581-581b
 —, M. H., 56 581c, 471 581c
 —, S. L. S., 44 350b, c, 467 350b, c
 Thompson, C. D., 183 192, 464 192
 Tichotsky, N., 108 289, 305 289, 466 289
 Tiemann, F., 76 582, 583, 279 582, 583, 471 582, 583
 Tiffeneau, M., 161 584, 191 585, 367 584, 387 585, 471 584, 585
 Tilden, W. A., 141 13, 14, 343 13, 14, 461 13, 14
 Tilicheev, M. D., 60 497, 64 497, 469 497
 Tischenko, V. E., 143 586, 333 586, 335 586, 337 586, 471 586
 Tizard, H., 95 224, 465 224
 Todd, S. S., 59 586a, 471 586a
 Toehl, A., 155 245, 156 245, 357 245, 359 245, 361 245, 465 245
 Toivonen, N. J., 121 587, 588, 317 587, 471 587, 588
 Tolman, R. C., 26 589, 471 589
 Tolpin, J. G., 426
 Tomi, W., 213 481, 399 481, 469 481
 Trakhtenberg, D. M., 44 347, 467 347
 Trautz, M., 55 590, 95 590, 245 590, 291 590, 471 590
 Treadwell, F. P., 471 590a
 Treibs, W., 148 591, 353 591, 471 591
 Tritzsch, W., 192 526, 389 526, 470 526
 Tsao, J. C., 184 592, 385 592, 471 592
 Tschitschibabin, A. E., 159 593, 471 593
 Turk, A., 74 593a, 75 593a, 76 593a, 275 593a, 277 593a, 279 593a, 471 593a
 Turova-Pollak, M. B., 44 594a, 94 675, 98 595-593a, b, 675, 99 593c, 674, 675, 100 675, 102 597, 674, 103 593a, b, 599, 106 594, 106 598aa, 112 673, 113 673, 674, 676, 114 677, 293 595, 295 596-593a, b, c, 297 674, 299 675, 301 597, 674, 303 598aa, ab, 303 599, 309 673, 674, 676, 677, 471 594-599, 472 673-674, 473 675-677
 Tuzson, P., 80 660, 661, 133 661, 281 660, 661, 283 660, 661, 325 661, 327 661, 472 660, 661
 Twigg, G. H., 55 600a, 56 600, 600a, 245 600, 247 600a, 471 600, 600a
 Tzurikov, F. F., 44 348, 161 348, 367 348, 467 348

U

Ubbelohde, L., 421 600b, 422 600b, 471 600b
 Uchida, S., 123 601, 471 601
 Ulffers, F., 143 601a, 339 601a, 341 601a, 449, 450, 471 601a
 Unger, F., 94 602, 471 602
 Universal Oil Products Co., 29 284, 604, 605, 31 605, 32 603, 605, 40 232a, 59 609a, 60 581a, 69 581a, 221 284, 604, 605, 231 603, 605, 233 232a, 253 581a, 265 581a, 426, 432, 452, 465 232a, 466 284, 471 581a, 603-603, 609a
 Uota, H., 149 606, 150 409, 410, 355 409, 468 409, 410, 471 606
 Urech, C., 57 64, 462 64
 Urushibara, Y., 166 607, 608, 167 607, 609, 371 607, 608, 373 607, 608, 471 607-609

V

Vaala, G. T., 155 415, 357 415, 359 415, 361 415, 468 415
 Van Arsdell, P. M., 26 160, 29 160, 37 159a, 155 160, 201 160, 463 159a, 160
 van der Zijden, M. J., 37 561a, 38 561a, 69 561a, 265 561a, 470 561a
 van Emster, K., 119 369, 370, 122 369, 143 369, 370, 317 369, 467 369, 370
 van Lookeren Campagne C. Jzn., W., 44 70, 71, 462 70, 71
 van Peski, A. J., 58 420, 59 609a, 249 420, 251 609a, 439, 445, 451, 455, 458, 468 420, 471 609a
 van Risseghem, H., 61 609aa, 471 609aa
 van Veen, A. G., 131 495, 325 495, 469 495

Vaughan, W. E., 56³⁰⁵, 58^{304a}, 62^{140a}, 305, 463^{140a}, 466^{304a}, 305
 Vavon, G., 119^{609b, c}, 471^{609b, c}
 Veijola, T., 121⁵⁸³, 471⁵⁸³
 Venable, C. S., 118⁶¹⁰, 128⁶¹⁰, 140⁶¹⁰, 143⁶¹⁰, 311⁶¹⁰, 323⁶¹⁰, 335⁶¹⁰, 471⁶¹⁰
 Verheus, J., 31^{135a, 529a}, 32^{529a}, 33^{529a}, 34^{529a}, 49^{135a, 529a}, 59^{529a}, 63^{529a}, 65^{529a}, 98^{529a}, 100^{529a}, 102^{529a}, 103^{529a}, 126^{529a}, 225^{135a, 529a}, 227^{529a}, 233^{529a}, 235^{529a}, 237^{529a}, 249^{529a}, 259^{529a}, 261^{529a}, 293^{529a}, 299^{529a}, 301^{529a}, 303^{529a}, 319^{529a}, 463^{135a}, 470^{529a}
 Visser, G. H., 455
 Vogel, A. I., 102^{128, 611, 612}, 301^{128, 611}, 463¹²⁸, 471⁶¹¹, 472⁶¹²
 Voht, G., 167⁵⁷⁰, 369⁵⁷⁰, 375⁵⁷⁰, 471⁵⁷⁰
 Vorlaender, D., 173⁶¹³, 379⁶¹³, 472⁶¹³
 Vsevolozhskaya, E. V., 99^{593c}, 295^{593c}, 471^{593c}

W

Wadsworth, F., 431
 Wagner, G., 119, 143⁶¹⁴, 472⁶¹⁴
 —, R. B., 64⁶⁴², 472⁶⁴²
 Walbaum, H., 146⁶⁵, 147⁶⁵, 462⁶⁵
 Walden, 57
 Walker, J., 148⁴⁷⁰, 469⁴⁷⁰
 —, J. F., 190⁵³⁰, 387⁵³⁰, 470⁵³⁰
 —, W., 146⁶³³, 147⁶³³, 353⁶³³, 472⁶³³
 Wallach, O., 76⁶³², 109^{623, 629, 630}, 110^{627, 628, 631}, 111^{624, 626}, 115⁶²², 116^{621, 622}, 118⁶²⁵, 119⁶²⁵, 120^{615, 625}, 128⁶¹⁵, 129^{616, 617, 618}, 130⁶²⁰, 135^{617, 619}, 140^{615, 616, 617}, 141^{615, 616, 617}, 144^{620a}, 146⁶³³, 147⁶³³, 279⁶³², 305^{623, 624, 626, 627, 628, 629, 630, 631}, 311^{620a, 622}, 313⁶²⁵, 323^{615, 617, 620}, 329^{617, 619}, 331⁶¹⁵, 341⁶¹⁵, 343^{616, 617}, 345^{615, 616}, 353⁶³³, 472⁶¹⁵⁻⁶³³
 Wallis, E. S., 27⁶³⁴, 66⁶³⁵, 472^{634, 635}
 Walpole, A. L., 44^{350c}, 115³⁵¹, 123³⁵², 309³⁵¹, 467^{350c, 351, 352}
 Wang, A. B., 131³⁵³, 145³⁵³, 323³⁵³, 351³⁵³, 467³⁵³
 Washburn, E. W., 21⁶³⁶, 472⁶³⁶
 Waterman, H. I., 122⁶³⁷, 317⁶³⁷, 472⁶³⁷
 Webel, F., 71⁶³⁸, 84⁶³⁹, 271⁶³⁹, 287⁶³⁹, 472^{638, 639}
 Wehrli, S., 80²⁹⁵, 466²⁹⁵
 Weiss, H., 168⁵², 169⁵³, 170^{54, 55}, 172⁵¹, 188⁵⁴, 379⁵¹, 461⁵¹, 462⁵²⁻⁵⁵
 Weitzenboeck, R., 94⁵²³, 470⁵²³
 Weizmann, A., 213⁵⁶, 399⁵⁶, 462⁵⁶
 —, C., 195⁶⁴⁰, 197⁶⁴⁰, 389⁶⁴⁰, 472⁶⁴⁰
 Went, F. W., 428
 West, S. D., 21^{91a}, 462^{91a}
 Wetmore, F. E. W., 56^{581c}, 471^{581c}
 Wettstein, A., 80²⁹⁵, 466²⁹⁵
 Wheeler, W. R., 64⁶¹², 472⁶¹²
 Wheland, G. W., 26^{433, 610a}, 468⁴³³, 472^{610a}

Whitaker, J. S., 64⁶⁴², 472⁶⁴²
 White, R. V., 176^{316a}, 190^{316a}, 381^{316a}, 387^{316a}, 466^{316a}
 Whitmore, F. C., 64⁶⁴², 65³²⁹, 66^{329, 643}, 93⁶⁴¹, 261³²⁹, 263³²⁹, 466³²⁹, 472⁶⁴¹⁻⁶⁴³
 Wibaut, J. P., 21^{643a}, 102⁶⁴⁴, 299^{643a}, 472^{643a}, 644
 Wiegand, C., 164⁶⁴⁵, 472⁶⁴⁵
 Wieland, H., 44^{645a}, 159⁶⁴⁶, 365⁶⁴⁶, 472^{645a, 646}
 Willemart, A., 183^{647, 648}, 383^{647, 648}, 472^{647, 648}
 Williams, D., 70⁶⁴⁹, 472⁶⁴⁹
 —, J. H., 131³⁵³, 145³⁵³, 323³⁵³, 351³⁵³, 467³⁵³
 Willstätter, R., 106⁶⁵⁰, 303⁶⁵⁰, 472⁶⁵⁰
 Wilson, E., 21⁶⁵¹, 26¹⁶⁰, 29¹⁶⁰, 64⁶⁵¹, 155¹⁶⁰, 201¹⁶⁰, 463¹⁶⁰, 472⁶⁵¹
 Windemuth, E., 119^{2a, b}, 461^{2a, b}
 Winkler, K., 55⁵⁹⁰, 95⁵⁹⁰, 245⁵⁹⁰, 291⁵⁹⁰, 471⁵⁹⁰
 Winter, D., 171⁵⁷, 176⁵⁷, 379⁵⁷, 381⁵⁷, 462⁵⁷
 Wislicenus, J., 84⁶⁵³, 165⁶⁵², 285⁶⁵³, 369⁶⁵², 371⁶⁵², 472^{652, 653}
 Wittig, G., 177⁶⁵⁴, 381⁶⁵⁴, 472⁶⁵⁴
 Wolff, W., 44⁴⁶⁷, 118⁴⁶⁶, 140⁴⁶⁶, 311⁴⁶⁶, 469^{466, 467}
 Wollschitt, H., 166⁶⁸⁰, 369⁶⁸⁰, 473⁶⁸⁰
 Wood, J. E., 155⁴¹⁶, 468⁴¹⁶
 —, III, J. E., 32^{357a}, 231^{357a}, 467^{357a}
 Wright, G. F., 126⁶⁵⁵, 166⁶⁵⁵, 472⁶⁵⁵
 Wüest, H.-M., 187⁶⁵⁶, 188⁶⁵⁶, 385⁶⁵⁶, 387⁶⁵⁶, 472⁶⁵⁶
 Würtz, A., 63⁶⁵⁷, 408, 472⁶⁵⁷

Y

Yarnall, W. A., 456
 Yohe, R. V., 26²⁶⁰, 465²⁶⁰
 Young, W. G., 55⁶⁵⁸, 472⁶⁵⁸
 Yuriev, Y. K., 42⁶⁵⁹, 106³⁴⁹, 239⁶⁵⁹, 303³⁴⁹, 467³⁴⁹, 472⁶⁵⁹

Z

Zechmeister, L., 80⁶⁶⁰, 661, 133⁶⁶¹, 281^{660, 661}, 283⁶⁶⁰, 283⁶⁶¹, 325⁶⁶¹, 327⁶⁶¹, 428, 472^{660, 661}
 Zeitschel, O., 143⁶⁶², 144⁶⁶², 347⁶⁶², 472⁶⁶²
 Zelinsky, N. D., 44^{663a, b}, 664, 665, 669a, 671a, b, 67^{12a}, 69⁶⁷⁰, 94⁶⁷⁵, 98⁶⁷⁵, 99^{674, 675}, 100⁶⁷⁵, 102⁶⁷⁴, 103⁵⁹⁹, 105⁶⁷¹, 106⁶⁶⁷, 108⁶⁷², 109⁶⁶⁸, 112^{671c, 673}, 113⁶⁷³, 113^{674, 676}, 114⁶⁷⁷, 118⁶⁶³, 121⁶⁶⁹, 125⁶⁶⁵, 126^{12a, 665}, 127⁶⁶⁶, 140⁶⁶³, 141^{669a}, 263^{12a}, 265⁶⁷⁰, 295^{12a}, 297⁶⁷⁴, 299⁶⁷⁵, 301^{12b, 674}, 303⁶⁷¹, 305^{663, 672}, 307^{671c}, 309^{673, 674, 676, 677}, 317⁶⁶⁹, 319^{12a, 665}, 321⁶⁶⁶, 345^{669a}, 461^{12a, 12b}, 471⁶⁹⁹, 472⁶⁶³⁻⁶⁷⁴, 473⁶⁷⁵⁻⁶⁷⁷
 Ziegler, K., 135²³, 136²³, 137²³, 166⁶³⁰, 174⁶⁷⁹, 175⁶⁷⁹, 188⁶⁷⁸, 329²³, 369⁶³⁰, 379⁶⁷⁹, 387⁶⁷⁸, 461²³, 473⁶⁷⁸⁻⁶³⁰
 Zilberman-Granovskaya, 106⁶³¹, 473⁶³¹
 Zimmermann, W., 146⁴⁸³, 469⁴⁸³
 Zwecker, O., 193^{57a}, 389^{57a}, 462^{57a}

Subject Index

A

- Abietic acid, 119, 314
 Acetic acid, action of on
 biphenylenediphenylbutadiene, 190, 386
 bornyl chloride, 120
 butenyl-methyl-dihydrophenanthrene, 196, 390
 cadinene, 147, 352
 α -camphorene, 132, 324
 Δ^1 -carene, 145, 350
 caryophyllene, 146, 352
 dimethylmethylene-cyclohexadiene, 135, 328
 dimethyloctadiene, 76, 278
 dimethyloctatriene, 77, 280
 dimethylundecatriene, 78, 280
 farnesenes, 79, 280
 gurjunene, 148, 352
 methyl-benzyl-isopropenyl-cyclohexadiene, 213, 398
 methylene-methyl-dihydronaphthalene, 191, 388
 methyl-phenyl-isopropenyl-cyclohexadiene, 213, 398
 oleanene, 151, 354
 pentaphenylpropene, 169, 376
 pentenes-2, 61, 256
 phenethylcyclohexene, 203, 392
 phenethylindene, 207, 394
 phylocladene, 151, 354
 α -pinene, 143-144, 336, 338, 342, 346, 348
 β -pinene, 118, 312
 sabinene, 115, 310
 tetraphenyl-butadiene, 176, 380
 butene, 171, 376
 di-tert-butyl-hexatetraene, 179, 380
 propadiene, 173, 378
 (tri)alkyl-tetrahydronaphthylethyl-indene, 210
 triphenyl-butadiene, 175, 378
 naphthyl-propadiene, 174, 378
 propargyl-diphenyl-indene, 182, 183, 382
 zingiberene, 131, 324
 Acetic anhydride, action of on
 α -pinene, 143, 144, 336, 346, 348
 squalene, 79
 1,1,3-triphenylbutadiene-1,2, 174, 175, 378
 Acetone, 322
 Acetophenone, 330
 Acid salts, 117, 143, 312, 338, 340
 Acids (*See also* Acetic acid, Hydrogen chloride, Phenols, etc.), 117, 130, 143, 310, 312, 322, 338
 complex, 117, 143, 312, 338, 340
 organic, 118, 119, 144, 146, 312, 314, 338-350
 Adkins' copper chromite, action of on
 cyclohexane, 294
 octahydrophenanthrene, 388
 α -pinene, 141, 334
 Adsorption, 133, 324, 326
 Aging, 14, 133, 199, 200, 254
 Aircraft, and octane number, 20
 Alapaevsk bauxite, 143, 332, 334
 Alcohol, action of on
 alkynes, 89
 d-2,4-cholestadiene, 354
 isostilbene, 368
 d-1-methyl-4-isopropylcyclohexenes-2 and -3, 320
 phylocladene, 354
 α -pinene, 340, 342, 344
 α -selinene, 352
 α -thujene, 330
 Alcoholic potash (*See* Potassium hydroxide, alcoholic; Potassium methoxide),
 definition, 70
 Alcoholic soda (*See* Sodium hydroxide, alcoholic; Sodium isoamylate; Sodium methoxide)
 Alkadienes, 51, 70
 1,2- from alkynes-1, 81, 285, 287
 isomerization, 70-77, 268, 274
 Alkadienes, allenic, from non-allenic, 77, 277
 isomerizations, 70, 73, 268
 Alkadienes, conjugated, from allenic alkadienes, 73, 269-273
 from non-allenic alkadienes, 77, 275-279
 Alkadienes, non-allenic, isomerizations, 73, 77, 274-279
 Alkadienyl benzenes, 173-177, 378-381
 Alkadiynes, 81, 86-90, 286-289
 Alkalies, action of on
 methylenecyclobutane, 108, 304
 phenylpropenes, 161, 366
 Alkanes (*See also* Gasoline, Hydrocarbons, Petroleum)
 analysis of mixtures, 21, 23, 24, 407-425
 from cyclohexanes, 99-103, 295-303
 higher, from octane, 39, 241
 isomerizations, 24, 28, 29, 31, 33, 35, 37, 40, 41, 42, 218-242
 methods of study of, 21
 number of, 22, 23
 Alkapolyenes, 51, 77-80, 280-283
 Alkapolyenyl benzenes, 177-180, 380-382
 Alkapolyynes, 86-90, 286-289
 Alkenes (*See also* Hydrocarbons)
 identification of isomers, 55
 isomerizations, 51-69, 244-267
 Alkenyl benzenes, 160-173, 366-379
 Alkyl benzenes, 152, 356-365
 Alkyl bromides, 33, 234
 Alkyl chlorides, action of on
 n-heptane, 35, 236
 n-hexane, 33, 234
 n-octane, 240
 n-pentane, 31, 230
 Alkynes (*See also* Hydrocarbons),
 from allenic alkadienes, 70-73, 269
 isomerizations, 81-90, 284-289
 Alkynyl benzenes, 180-185, 382-385
 Allene (-Propadiene), 70, 81, 268, 269, 285
 Alloöcimene, 77, 78, 280, 281
 from α -pinene, 141, 142, 331, 333, 335
 from β -pinene, 117, 118, 311
 Allylbenzene, 161, 366, 367
 Allylcyclohexane, 107, 110, 304
 Allylene (-Propyne), 70, 81, 269, 284, 285
 Allylmethylbenzenes, 163-164, 368
 1-Allylnaphthalene, 191, 386
 9-Allylphenanthrene, 196, 388
 Allylpropenyl (Hexadiene-1,4), 73, 74, 274, 275, 277
p-Allylpropenylbenzene, 164, 369
 Allyltoluenes, 163-164, 368
 Alpha particles, 81
 Altitude, aircraft, effect of octane number on, 20
 Alumina, 29, action of on
 allylnaphthalene, 191, 386
 allyltoluenes, 163, 164, 368
 butanes, 29, 220, 222
 butenes, 56, 58, 246, 248
 carotenes, 132-134, 325-326
 cyclanes, 96, 108, 290-294, 304
 cyclenes, 125, 318, 324, 326
 cyclohexane, 99, 294
 cyclohexene, 125, 318
 cyclopropanes, 96, 290, 292
 n-decane, 42, 242
 diallylbenzene, 164, 368
 dimethylbutene, 65, 260
 dimethylhexadiene, 76, 278
 heptadiene, 74, 276
 heptenes, 67, 262
 hexadecene, 69, 264, 266

- Alumina, hexadienes, 74, 274, 276
 hexenes, 64, 258, 260
 action of on isoamylalcohol, 62
 isobutane, 29, 30, 220, 222
 methylbutadiene, 71, 270
 methylbutenes, 61, 256, 258
 methylbutyne, 84, 286
 methylcyclobutane, 97, 292
 methylenecyclobutane, 108-109, 304
 methylenecyclopropane, 108, 304
 methylheptadiene, 75, 276
 methylhexadienes, 75, 76, 276
 methylhexenes, 67, 262
 methylpentenes, 64, 260
 octadiene, 75, 276
 n-octane, 42, 238
 octenes, 68, 69, 264
 pentenes, 60, 252, 254, 256
 phenylbutene, 161, 366
 phenylpropene, 161, 366
 α -pinene, 140, 143, 332, 334
 pseudo- α -carotene, 132-134, 324
 Aluminosilicic acids, 117-118, 143, 312, 340
 Aluminum, action of on
 decalin, 114, 308
 l- α -pinene, 332
 Aluminum bromide, action of on
 n-butane, 28, 30, 218
 cyclohexanes, 99-102, 292, 296, 298, 300
 decalin, 113, 308
 n-hexane, 33, 234
 hydrindane, 113, 308
 isobutane, 30, 218, 226
 isohexanes, 33, 34, 234, 236
 isopentanes, 32, 33, 228, 232, 234
 n-octane, 40, 240
 n-pentane, 31, 228, 232
 Aluminum chloride, action of on
 alkanes, 24, 28-40, 50, 218-242
 alkylbenzenes, 155-158, 356-364
 aromatic cyclenes, 201-213, 392-396
 benzene, 63, 154
 bicyclanes, 113-115, 308
 cycloheptane, 106, 302
 cyclohexanes, 94, 99-106, 292, 298-302
 cyclopentanes, 97-99, 292, 294
 decalin, 113-115, 308
 diphenylmethylpentene, 172, 378
 isoalkanes, 30-40, 218-242
 methylbutene, 63, 256
 octahydroanthracene, 193-194, 196, 388
 octahydrophenanthrene, 193-194, 196, 388
 tetradecahydroanthracene, 122, 316
 β -vetivane, 115, 308
 Aluminum phosphate, action of on
 butene-1, 56, 244
 α -pinene, 143, 334
 Aluminum silicates (*See also* Alumina, Silica, and specific aluminum silicates), 246, 248, 252, 264, 266
 Aluminum sulfate, 56, 58, 62, 65, 244, 256, 260
 Ammonium molybdate, 312, 338
 Ammonium tungstate, 312, 338
 Ammonium vanadate, 312, 338
n-Amylcyclohexane, 302
n-Amylcyclopentane, 98, 294
 Analysis, of alkanes, 21, 23, 24, 407-425
 Aniline, 322
 Anthracenes, 193-198, 389
 Antiknock value, 7, 19, 38
 Antimonic acids, 143, 312, 338, 340
 Antimony pentachloride, 23, 407-419
 Antimony trichloride, 407-417
 β -Apo-4-carotenal, 327
 Apophyllite, 218
 Aromatics (*See also* Aromatization, Hydrocarbons), 152, 356
 alkadienyl benzenes, 173, 378
 alkapolyenyl benzenes, 177, 380
 alkenyl benzenes, 160, 366
 alkyl benzenes, 152, 356
 alkynyl benzenes, 180, 382
 anthracenes, 193, 388-389
 condensed, 185, 384
 fluorenes, 189, 385, 386, 387
 indanes, 185, 384, 386, 387
 Aromatics, indenenes, 185, 384, 385, 386, 387
 naphthacenes, 197, 390
 naphthalenes, 190, 386, 387, 388-389, 392-394, 396-397
 phenanthrenes, 196, 388, 389-394, 396
 Aromatization, 42, 44, 134-139, 239, 243, 295, 297, 319, 323, 327-329, 331, 333, 335, 341, 343, 345, 349
 Arsenic acid, 128, 140, 322, 340
 Arsenomolybdic acid, 143, 312, 340
 Ascaridole, 166, 167, 372, 374
 Atoms, 18

 B
 Bauxite, 56, 143, 244, 332, 334
 Bentonite, 218
 Benzene, action of on
 hexaphenylethane, 364
 isostilbene, 370-374
 stilbene, 374
 alkylation, 96, 154
 as solvent, 79, 280, 282, 314, 324, 326, 350
 chlorination, 415
 from ethylbenzene, 156
 measurements, 422, 424
 isomerization, 153-154
 Benzene sulfonic acid, 244, 346
 Benzhydryl . . . , *See* Benzohydryl . . .
 Benzine, 324, 326
 3-Benzohydryl-1-benzylidene-indene, 188, 386
 1-Benzohydryl-3-sec-butyl-indene, 187, 384
 3-Benzohydrylidene-1-sec-butyl-indene, 187, 385
 9-Benzohydrylidene-10-phenyl-9,10-dihydro-anthracene, 194, 195, 388
 Benzohydrylindenes, 186, 384, 385
 9-Benzohydryl-10-phenylanthracene, 194, 195, 389
 9-Benzohydryl-10-phenyl-9,10-dihydroanthracene, 195
p-Benzohydryl-tetraphenylmethane, 159, 365
 Benzoic acid, action of on
 isostilbene and stilbene, 167, 374
 d-limonene, 322
 methylenecyclohexane, 109, 304
 α -pinene, 143, 144, 346, 348
 l- β -pinene, 118, 314
 vinylidenecyclohexane, 110, 304
 Benzoquinone, 140, 330
o-Benzoylbenzoic acid, 143, 348
 Benzoyl peroxide, 166-167, 372, 374
 Benzylallene,
 (-4-Phenylbutadiene-1,2), 181, 383
 3-Benzyl-1-benzylidene-indene, 187, 385
 1-Benzyl-2,2-bis(β , β -diphenylvinyl)ethylene, 177-178, 381
 1-Benzyl-2,3-diphenylindane, 171-172, 176, 377, 379, 381
 1-Benzyl-2,3-diphenylindene, 176, 381
 3-Benzyl-1-diphenylmethylene-indene, 188, 387
 1-Benzylidene-3-benzohydryl-indene, 188, 386
 1-Benzylidene-3-benzylindene, 187, 385
 1-Benzylidene-2,3-diphenylindane, 176, 381
 1-Benzylidene-3-isopropylbenzylindene, 187-188, 387
 1-Benzylidene-3-*p*-methylbenzyl-indene, 187-188, 387
 1-Benzylindene, 186, 384
 3-Benzylindene, 186, 385
 3-Benzyl-1-isopropylbenzylidene-indene, 187-188, 387
 3-Benzyl-1-*p*-methylbenzylidene-indene, 187-188, 387
 1-Benzylidene-3-*p*-methylbenzyl-indene, 187-188, 386-387
 Beryllium oxide, 67, 126, 262, 318
 Bicyclanes with saturated side-chains, 91, 112-115, 308-309
 with unsaturated side-chains, 115-121, 310-315
 Bicyclenes, with saturated side-chains, 125, 139, 330
 with unsaturated side-chains, 146, 352
 Bicyclacamphorenes, 132, 325
 Bicyclodecanes (*See also* Decalin), 112-115, 177, 308, 309, 378
 Bicyclodecenes (*See also* Octalin), 131, 145-146, 323, 350, 351

- Bicyclodienes, 147, 352
 Bicycloheptanes, 109, 112, 116-121, 310-314
 Bicyclohexanes, 115, 120, 121, 310
 Bicycloisoprenemyrcene, 131, 325
 Bicyclononanes, 113, 308, 309
 Bicyclooctanes, 106, 113, 303, 308, 309
 Bicyclopaffins, with saturated side-chains, 91, 112-115, 308-309
 with unsaturated side-chains, 115-121, 310-315
 1-(*o*-Biphenyl)cyclopentene-1, 201, 392
 1-Biphenylene-4-phenylbutene-1, 189-190, 387
 1-Biphenylene-4-phenylbutene-2, 189-190, 386, 387
 1-Biphenylene-3-phenylindene, 189, 386
 Bisabolenes, 78, 79, 281
 α -Bisabolyl acetate, 79, 281
 Bis-1,1'-(1,3-diphenylindenyl), 182-183, 383
 1,3-Bis-(4-[9-octracetyl]-butyl)benzene, 193-194
 Bis-(trimethylcyclohexenyl)-tetramethyloctadecanone (- β -Carotene), 132-134, 324-327
 Bleaching earth, 126, 310, 318, 320
 Bobrik clay, 334
 Boracetic acid, 143, 312, 340
 Boracetic anhydride, 346
 Borates, 56, 244
 Boric acid, 143, 312, 340, 348
 Boric anhydride, 143, 348
 Borneol, 343, 347, 351
 Bornyl chloride, 119, 120, 341
 Bornyl esters and ethers,
 from α -pinene, 143, 144, 145, 337, 341, 345, 347, 349, 351
 from β -pinene, 118, 119, 120, 315
 Boron fluoride, action of on
 isostilbene, 165, 167, 370
 n-pentane, 32, 230
 for alkylation of alkanes, 26
 Borophosphoric acids, 143, 312, 340
 Borotungstic acids, 143, 312, 340
 Bromine, 165, 166, 370
 Bromobenzene, 336
 Butadiene-1,2, from butyne-1 and -2, 84, 285
 isomerizations, 70, 268
 Butadiene-1,3, from butadiene-1,2, 70
 from butyne-1, 84, 285
 from methylenecyclopropane, 108, 305
 from 1-methylcyclopropene-1, 125, 319
n-Butane, antiknock value, 38
 from isoamylcyclohexane, 103, 303
 isomerizations, 7, 27-30, 40, 218-228
 (thermodynamic data), 30, 31, 33, 43-50
 Butanes, from *n*-pentane, 32, 229
 thermodynamic data, 43-50
 Butanol-2, 96
 Butene, 70, 269
 Butene-1, 51-53, 55-59, 244-252
 Butene-2,
 from butene-1, 51-53, 55-59, 244-252
 from methylcyclopropane, 96, 293
 Butenes, isomerizations, 55, 244
 Butenes-2, mechanism of isomerization, 51, 55, 56-59, 167, 173
 Butenylbenzenes, 161-162, 366, 367
 1-(3-Butenyl)cyclohexanol-1, 131
 1-(3-Butenyl)cyclohexene-1, 131, 145, 322
 1-(3-Butenyl)-2-methyl-3,4-dihydrophenanthrene, 196-197, 388
tert-Butylacetylene(-3,3-Dimethylbutyne), 85, 286
n-Butylallene (-Heptadiene-1,2), 72, 85, 270, 287
tert-Butylallene (-4,4-Dimethylpentadiene-1,2), 72-73, 137, 181-182, 270
tert-Butylbenzene, 32, 230, 232
sec-Butylbenzohydrylindenes, 187, 384, 385
 (*tert*-Butyl)(*tert*-butylethynyl)(phenyl) methyl bromide, 183
n-Butyl chloride, 35, 236
 Butylcyclohexanes, 103, 105, 302
 Butylcyclopentanes, 98, 294
 Butyl dimethylbenzene (See Dimethyl-butylbenzene)
 1-Butyl-2-methylphenanthrene, 196-197, 389, 391
 Butyne-1, from butadiene-1,2, 70, 269
 from butyne-2, 84, 285
 isomerizations, 82, 84, 284
 Butyne-2, from butadiene-1,2, 70, 269
 from butyne-1, 82, 84, 284, 285
- C**
- Cadinenes, 79, 147, 148, 352, 353
 Calcium chloride, 380
 Calcium hydroxide, 134, 326
 Calcium oxide, 56, 85, 244, 286
 Calcium phosphate, 143, 334, 338
 Camphene,
 action of phosphoric acid, 116, 310
 from α -pinene, 141, 143-146, 333-351
 from β -pinene, 117-120, 311, 313, 315
 from tricyclene, 121, 317
 Camphene hydrochloride, 119, 120
 Camphorenes, 117, 132, 324-325
 Carbon, action of on
 n-butane, 29, 220
 butenes, 248
 n-octane, 42, 238
 n-pentane, 32, 230
 α -pinene, 140-143, 330, 332
 Carbon disulfide, action of on
 aromatic cyclenes, 201-212, 392, 394, 396
 condensed aromatics, 388
 isostilbene, 370
 Carbon tetrachloride, 370
d- Δ^3 -Carene, 145, 350
d- Δ^4 -Carene, 145, 350
 Carius tube, 330
 β -Carotenal, 327
 Carotenes, 132-134, 324-327
 Carotenoids, 132-134, 324-327
 Carvomenthene, 126, 318, 320
 Caryophyllenes, 146, 147, 352
 Caryophyllene hydrate, 146
 Catalysts, for isomerization (See Isomerization)
 Catechol, 167, 370, 372, 374
 Cedrene, 148, 352
 Chamotte, 58, 250, 252
 Charcoal, action of on
 allyltoluene, 368
 n-butenes, 58, 248
 butenyl-methyl-dihydrophenanthrene, 388
 cyclofenchene, 316
 1-ethynylcyclohexene-1, 326
 4-phenylbutene-1, 366
 3-phenylpropene-1, 161, 366
 α -pinene, 332
 spirodecane, 306
 hydrogenation by platinized, 67
 Chemical industry, and isomerization of hydrocarbons, 7, 13
 Chlorination,
 of alkane molecules, 407-419, cf. 23
 of benzene, 415
 of ethylene, 415
 Chloroacetic acid, 140, 143, 346
 Chloroform, 354
 2-Chloro-2-methylbutane, 415
 3-Chloro-3-methylbutene-1, 73
 2-Chloro-2-methylpropane, 415
 Chlorosulfonic acid, 32, 230
 Cholestadienes, 150, 354
 Chromatography, 133-134, 324, 326
 Chromic acid, 151, 354
 Chromium oxide (See also Copper chromite),
 action of on
 alkenyl benzenes, 172, 366
 alkynyl benzenes, 180-181, 382
 hexadiene-1,5, 74, 274
 2-methylbutene-2, 258
 pentene-2, 61, 254
 4-phenylbutene-1, 161, 366
 4-phenylbutyne-1, 180-181, 382
 5-phenylpentene-1, 162-163, 366
 3-phenylpropene-1, 161, 366
 Chromium phosphates, 266
 Chromium sulfates, 266
 Chromoxalic acids, 143, 312, 338, 340
 Cineol, 141, 343
 Citronellenes, 78
 Clay (See also Alumina, Aluminum silicate, Chamotte, Fire-bricks, Kaolin, Kaolinite, Silicates), action of on
 alkanes, 218, 222, 230
 butenes, 58, 248
 carvomenthene, 320

Clay, dipentene, 128, 129, 322
 3-phenylpropene-1, 161, 366
 α -pinene, 143, 332, 334, 336
 β -pinene, 310
 Clovene, 146, 147, 353
 Clove oil, 146
 Cobalt, 308
 Cobalt oxide, 61, 254, 258
 Cobalt phosphates, 266
 Cobalt silicate, 192, 386
 Cobalt sulfate, 143, 266, 336
 Cobalt, sulfur compounds, 98, 101, 292, 296
 Cobalt-thorium catalyst, Fischer and Koch's, 141, 334
 Colophony, 119, 143, 314, 348
 Configurational notations, 78, 144
 Copper, action of on
 carvomenthene, 318
 n-hexane, 234
 isostilbene, 165, 166, 370
 methylbutenes, 256
 n-octane, 42, 238
 α -pinene, 142, 332, 340, 348
 β -pinene, 312
 Copper chromite, 141, 196, 334, 388
 Copper oxide, action of on
 carvomenthene, 320
 n-heptane, 41, 238
 d- α -pinene, 140, 334
 Copper phosphate, 126, 266, 318
 Copper silicate, 192, 388
 Copper sulfate, 37, 220, 266, 320
o-Cresol, 144, 348
 Cryptomerenes, 123
 Cryptomeria japonica, 123
 Curcumene, 138, 328
 Cyclanes,
 resembling lubricating oil, from alkenes, 257
 with saturated side-chains, 91
 isomerizations, 91-107, 290-303
 with unsaturated side-chains, 107
 isomerizations, 108-112, 304-307
 Cyclenes,
 with saturated side-chains, 125-127, 305, 318, 320
 with unsaturated side-chains, 127-134, 322-329
 Cyclization, 33, 63, 76-80, 106-108, 127, 129, 131-132, 145-147, 149-150, 160-163, 167-177, 179, 182-185, 190, 192-193, 195-199, 201-214, 428-429, 431-432.
 Cyclization followed by decyclization, 25, 27, 34, 36-37, 52-53, 66, 88, 94-95, 100, 125
 Cyclobutanes, 97, 292
 with unsaturated side-chains, 108-109, 304
 Cyclodienes,
 with saturated side-chains, 134, 328
 with unsaturated side-chains, 135, 328
 Cyclodihydromyrcene, 76-77, 279
 Cyclofenchene, 117-118, 121, 123, 316
 Cyclogeraniolenes, 76, 279
 Cycloheptadecane, 107
 Cycloheptane, 106, 302
 Cyclohexane,
 determination of methylcyclohexane in, 418
 from *n*-hexane, 33, 235
 from methylcyclopentane, 97-98, 293
 isomerizations, 91-94, 99-101, 103, 292-301, 428
 Cyclohexanes, 91-95, 99-106, 292-303
 with unsaturated side-chains, 107, 109-111, 304, 306
 Cyclohexene, 125-126, 318
 Cyclohexenes, 305
 9-Cyclohexenylphenanthrene, 207
 Cyclohexylacetylene, 110, 111, 304, 305
 4-Cyclohexylbutene-1, 108
 4-Cyclohexylbutyne-1, 305
 1-Cyclohexylbutyne-2, 304, 305
 Cyclohexylethylene, 110, 305
 Cyclohexylhexynes, 111, 306, 307
 Cyclohexylideneethylene, 111, 305
 Cyclohexylpentynes, 111, 304-307
 Cycloisoprenemyrcene, 131, 324
 Cyclolinaloolene, 76-77, 279
 Cyclomethylgeraniolene, 76-77, 279
 Cyclomyrcene, 78, 142, 281
 Cyclooctane, 106, 302
 Cyclopentadecane, 107

Cyclopentanes,
 from 1,3,5-trimethylcyclohexane, 103-104, 303
 isomerizations, 97-99, 292-301
 with unsaturated side-chains, 109, 304
 1,2-Cyclopentano-1,2,3,4-tetrahydrophenanthrenes, 201-202, 393
 Cyclopentenenes, from *d*-1-methyl-4-isopropylcyclohexene-3, 127, 321
 9,10-Cyclopentenophenanthrene, 196, 389
 1-Cyclopentyl-1,2,3,4-tetrahydronaphthalene, 201, 393
 Cyclopropane, 91, 93, 95-96, 290, 291
 Cyclopropanes with unsaturated side-chains, 108, 304
 Cyclosesquictronellene, 78
p-Cymene,
 from dipentene, 128-129, 323
 from methylenecyclobutane, 108-109, 305
 from α -pinene, 141, 331, 333, 335, 341, 343, 345, 349
 from *l*- α -pinene, 144-145, 332-333, 340-345, 348-349
 from α -thujene, 139, 331

D

d-, 78
 Dacrene, 149-151, 354, 355
 Decalin, 112, 113-115, 308
 as solvent, 177, 378
n-Decane, 42, 242
 Decenes, 69, 264
 Decyclization, 91, 93, 95-97, 108-109, 115-122, 125, 130, 139-145, 147-148, 153, 353
 Decyclization followed by cyclization, 93, 122, 125, 153, 189, 193-194, 196, 198
 Density, of alkanes, 420, 421-425
 Deoctahydro-tetraterpenes (-Carotenoids), 132-134, 324-327
 Deoxyquillaic acid, 430
 Depolymerization followed by polymerization, 53-54, 124, 159, 200
 Diallyl (-Hexadiene-1,5), 73, 74, 274-277
p-Diallylbenzene, 164, 368
 Diatomaceous earth (See Kieselguhr)
 Dibenzofluorene, 432
 1,2,3,4-Dibenzo-9-phenylfluorene, 189, 387
 Dibenzylene-diphenyl-cyclobutanes, 199, 390-391
 1,3-Dibenzylidene-indane, 187, 384
 1,2-Di-*tert*-butyl-1,2-di-*tert*-butylethynyl-di-phenylethane, 183
 1,1'-Di-*tert*-butyl-3,3'-diphenyl-1,1'-biindene, 179, 381
 1,2-Di-*tert*-butylethynyl-tetra-biphenylethane, 184
 1,2-Di-*tert*-butylethynyl-tetraphenylethane, 181-185, 382
 2,3-Di-*tert*-butyl-4-phenyl-1-(β,β -di-phenyl-vinyl)-naphthalene, 183-184. cf. 179
 3,4-Di-*tert*-butyl-1,1,6,6-tetraphenyl-hexatetraene-1,2,4,5, 179, 183-184, 380, 383, 385
 Dicyclohexyl, 99-100, 106, 299, 302, 303
 (*p*-[Di-cyclohexylmethyl]-phenyl)(phenyl)(di-cyclohexyl)-methane, 200
 Dicyclosqualene, 79, 281
unsym-Diethylallene (-3-Ethylpentadiene-1,2), 73, 272
 1,3-Diethylcyclohexane, 103, 105, 302
 Diethyl-dimethyl- (See Dimethyl-diethyl-)
 1,11b-Dihydro-7-benz[de]anthrene, 192, 389
 Dihydrobenzanthrenespirocyclohexane, 206, 395
 Dihydro-6-*meso*-benzanthrenespirocyclopentane, 203, 393
 Dihydrobenzanthrenespiromethylcyclohexane, 207, 395
 Dihydrocamphene, 112-113
 Dihydrocinnylidenefluorenes, 189-190, 386, 387
 2,3-Dihydro-1-cyclopenta[*l*]-phenanthrene, 196, 389
 Dihydro-cyclopenta[*l*]phenanthrene-spirocyclohexane, 206
 2,3-Dihydro-4'-isopropyl-7'-methyl-spiro[benzonaphthene-1,1'-indan], 209, 395
 Dihydrolinalyl acetate, 77, 279
 8,9-Dihydro-2'-methyl-spiro[β -acenaphthindan-3,1'-cyclohexane], 206, 395

- Dihydromyrcene, 76-77, 278
 Dihydronaphthalenes, 190, 386, 387
 7,8-Dihydrophenalyl-7-spirocyclohexane, 205, 395
 7,8-Dihydrophenalyl-7-spirocyclopentane, 201-202, 393
 1,2-Dihydro-4-(β -phenethyl)phenanthrene, 211, 396
 Dihydrotubrenes, 197, 199, 390, 391
 1,2-Dihydro-spiro[3-benz[e]indene-3,1'-cyclopentane], 201-202, 393
 2,3-Dihydro-spiro[benzonaphthene-1,1'-cyclohexane], 205, 395
 2,3-Dihydro-spiro[benzonaphthene-1,1'-cyclopentane], 201-202, 393
 3',4'-Dihydro-spiro[indan-1,1'(2')-phenanthrene], 211, 397
 Dihydroterpinolene, 111, 304
 1,3-Diiodopropane, 96, 291
 Diisobutenyl (-2,5-Dimethylhexadiene-1,5), 75-76, 278, 279
 Diisocrotyl (-2,5-Dimethylhexadiene-2,4), 75-76, 279
 Dimethylacetylene (-Butyne-2), 70, 82, 84, 269, 284, 285
unsym-Dimethylallene (-3-Methylbutadiene-1,2), 71-73, 84, 268, 270, 271, 287
 1,5-Dimethyl-5-allylcyclohexene-1, 78, 281
 Dimethylbenzenes (See also Xylene[s]), 152, 155, 156, 356-361
 Dimethylbicycloöctanes, 113-114, 309
 2,6-Dimethylbicyclo[3.2.1]octene-2, 129
 3,7-Dimethylbicyclo[4.2.0]octene-3, 129
 2,2-Dimethylbutane,
 antiknock value, 38
 from 2,3-dimethylbutane, 34, 237
 from *n*-hexane and 2-methylpentane, 33-35, 235
 isomerizations, 34, 236
 (thermodynamic data), 35, 43-50
 2,3-Dimethylbutane,
 analysis and determination, 408-414, 418
 antiknock value, 38
 from *n*-hexane and 2-methylpentane, 33-35, 235
 isomerizations, 28, 34, 236
 (thermodynamic data), 35, 43-50
 Dimethylbutenes, 65-66, 260, 262
 and aromatizations, 136-137
 1,3-Dimethyl-4-*n*-butylbenzene, 157-158, 362
 1,3-Dimethyl-4-*sec*-butylbenzene, 157, 362
 1,3-Dimethyl-4-*tert*-butylbenzene, 157, 362, 364
 1,3-Dimethyl-5-*sec*-butylbenzene, 157, 363
 1,3-Dimethyl-5-*tert*-butylbenzene, 157, 158, 363, 365
 3,3-Dimethylbutyne-1, 85, 286
 Dimethylcyclobutane, 97-100, 299
 1,1-Dimethylcyclohexane, 103, 302, 303
 1,2-Dimethylcyclohexane, 91, 94-95, 103, 104, 299, 303
 1,3-Dimethylcyclohexane, 91, 92, 94, 95, 98, 100, 101, 103, 104, 106, 295, 299, 302, 303
 1,4-Dimethylcyclohexane, 91, 98, 103, 104, 295, 302, 303
 1,2-Dimethylcyclopentane, 99, 102, 104, 294, 301
 1,3-Dimethylcyclopentane, 102, 104, 301
 Dimethylcyclopentene, 126, 319
 1,1-Dimethylcyclopropane, 97, 292
 1,2-Dimethylcyclopropane, 52, 92
 Dimethyldecalin, 115, 308, 309
 Dimethyldicyclopentyl, 100, 106, 299
 Dimethyl-diethyl-di(methyl-ethyl-pentynyl)-di(methylpentynyl)-hexadecatetraenediyne, 87, 289
 Dimethyl-diethyl-tetra-(methyl-ethyl-pentynyl)-dodecadiyne, 87, 288
 3,10-Dimethyl-3,10-diethyl-6,6,7,7-tetraphenyl-dodecadiyne-4,8, 184-185, 384
 1,2-Dimethyl-4-ethylbenzene, 136, 329
 1,1-Dimethyl-4-ethylidenecyclohexadiene-2,5, 136, 328
 1,2-Di-(3-methyl-3-ethylpentynyl-1)-tetraphenylethane, 184-185, 384
 2,6-Dimethylheptadiene-1,5, 76, 278
 2,5-Dimethylhexadiene-1,5, 75-76, 278, 279
 2,5-Dimethylhexadiene-2,4, 75-76, 279
 Dimethyl-hexahydrophenanthrene, 213, 399
 2,3-Dimethylhexane,
 antiknock value, 39
 2,5-Dimethylhexane,
 analysis and determination, 408-414, 418, cf. 24
 antiknock value, 39
 isomerization, 28
 3,4-Dimethylhexane, antiknock value, 39
 1-(1,5-Dimethyl-4-hexenylidene)-indene, 185, 384
 1,1-Dimethylindane, 162, 367
 1,3-Dimethyl-4-isobutylbenzene, 158, 362
 1,1-Dimethylisoprene (-2,4-Dimethylpentadiene-1,3), 72-73, 75, 137, 270, 271
d-1,2-Dimethyl-4-isopropenylcyclohexadiene-2,6, 137-138, 328
 1,2-Dimethyl-4-isopropylbenzene, 137-138, 329
 1,3-Dimethyl-4-isopropylbenzene, 157, 362
 1,3-Dimethyl-5-isopropylbenzene, 157, 363
 Dimethyl-isopropyl-bicyclodecane, 115, 308, 309
 Dimethyl-isopropyl-octahydro-naphthofluorene, 210, 397
 2,2-Dimethyl-3-methylene-bicyclo[2.2.1]heptane (See Camphene)
d-2,2-Dimethyl-5-methylene-bicyclo[2.2.1]heptane (- β -Fenchene), 116, 117, 120, 121, 310, 311, 317
 7,7-Dimethyl-2-methylene-bicyclo[2.2.1]heptane (- α -Fenchene), 117, 121, 310, 311, 317
 6,6-Dimethyl-2-methylene-bicyclo[3.1.1]heptane (- β -Pinene), 117-120, 130, 143-144, 310-315
 1,1-Dimethyl-4-methylene-cyclohexadiene-2,5, 135, 328
d-2,2-Dimethyl-5-methylene-norcamphane (- β -Fenchene), 116, 117, 120, 121, 310, 311, 317
 7,7-Dimethyl-2-methylene-norcamphane (- α -Fenchene), 117, 121, 310, 311, 317
 1,2-Dimethylnaphthalene, 191, 387
 1,6-Dimethylnaphthalene, 191, 386
 2,6-Dimethylnaphthalene, 191, 387
 2,5-Dimethyl-3-(β -1'-naphthylethyl)indene, 208, 394
 2,6-Dimethyl-3-(β -1'-naphthylethyl)indene, 209, 394
 2,7-Dimethyl-3-(β -1'-naphthylethyl)indene, 209, 394
 4,8-Dimethylnonatriene-1,3,7, 78, 280
 2,6-Dimethyloctadiene-2,6, 76-77, 278
 4a,11-Dimethyl-1,2,3,4,4a,11,12,12a-octahydrochrysene, 206, 395
 5,10a-Dimethyl-*as*-octahydrochrysene, 206, 395
 2,7-Dimethyloctane, 28
 2,6-Dimethyloctatriene-1,5,7, 77-78, 280, 281
 2,6-Dimethyloctatriene-2,4,6, 77-78, 280, 281
 4,4-Dimethylpentadiene-1,2, 72-73, 137, 181-182, 270
 2,4-Dimethylpentadiene-1,3, 72, 73, 75, 137, 270, 271, 276, 277
 2,4-Dimethylpentadiene-2,3, 72, 73, 75, 137, 270, 271, 276, 277
 Dimethylpentane, 35, 236
 2,2-Dimethylpentane,
 antiknock value, 38
 thermodynamic data, 43-50, 427
 2,3-Dimethylpentane,
 antiknock value, 38
 thermodynamic data, 43-50, 427
 2,4-Dimethylpentane,
 antiknock value, 38
 from *n*-heptane, 36, 237
 isomerizations, 41, 238
 (thermodynamic data), 43-50, 427
 3,3-Dimethylpentane,
 antiknock value, 38
 from *n*-heptane, 36, 237
 thermodynamic data, 43-50, 427
 4,4-Dimethylpentene-1, 72, 271
 Dimethylphenethylcarbinol, 162
 1,2-Dimethyl-3-(β -phenethyl)cyclohexadiene-1,3, 213, 398
 2,2-Dimethylpropane, 43-50
 1,2-Dimethyl-4-*n*-propylbenzene, 136, 329
 1,3-Dimethyl-4-*n*-propylbenzene, 157, 362
 1,1-Dimethyl-4-propylidenecyclohexadiene-2,5, 136, 328
 Dimethylrubrenes, 197, 390
 Dimethyl sulfate, 41, 170, 376
 4,10-Dimethyl-3,4,10,11-tetrahydro-2',1'-naphtha-1,2-fluorene, 208, 395

6,10-Dimethyl-3,4,10,11-tetrahydro-2',1'-naphtha-1,2-fluorene, 208, 395
 7,10-Dimethyl-3,4,10,11-tetrahydro-2',1'-naphtha-1,2-fluorene, 209, 395
 8,10-Dimethyl-3,4,10,11-tetrahydro-2',1'-naphtha-1,2-fluorene, 209, 395
 6,11a-Dimethyl-5,6,6a,11a-tetrahydro-11-naphtho-[2,1-a]-fluorene, 208, 395
 8,11a-Dimethyl-5,6,6a,11a-tetrahydro-11-naphtho-[2,1-a]fluorene, 208, 395
 9,11a-Dimethyl-5,6,6a,11a-tetrahydro-11-naphtho-[2,1-a]fluorene, 209, 395
 10,11a-Dimethyl-5,6,6a,11a-tetrahydro-11-naphtho[2,1-a]fluorene, 209, 395
 2,4-Dimethyl-3-(β -[5,6,7,8-tetrahydro-1-naphthyl]-ethyl)-7-isopropylindene, 210, 396
 1,3-Dimethyl-2,4,5-triphenylcyclopentanes, 199, 390, 391
 2,6-Dimethylundecatriene-2,5,8 (-Pseudoionane), 78, 280
 Dinaphthyl, 192, 388, 389
 Dinaphthyl-diphenyl-propadiene, 174, 378
 Dinitro-*o*-cresol, 144, 350
 2,6-Dinitro-*p*-cresol, 144, 350
m-Dinitrophenol, 144, 348
 Dipentene,
 from limonene, 128, 323
 from *d*- and *l*- α -pinene, 140, 141, 142, 144, 331-351
 from β -pinene, 117-118, 315
 isomerizations, 128, 129, 130, 322
 Dipentene dihydrochloride, 120, 129-130
 Dipentene monohydrochloride, 129-130, 341
 Diphenylamine, 370, 372
 1,2-Diphenyl-1-benzohydrylethylene, 169, 376
 2,3-Diphenyl-1-benzylidene-indane, 176, 381
 2,3-Diphenyl-1-benzylindane, 171-172, 176, 377, 379, 381
 2,3-Diphenyl-1-benzylindene, 176, 381
 Diphenylbromomethane, 167-168, 376
 1,4-Diphenylbutadiene-1,3, 175, 380, 381
 2,3-Diphenylbutanes, 159, 364, 365
 1,4-Diphenylbutatrienes, 177, 380, 381
 1,3-Diphenylbutene-1, 169, 376
 1,3-Diphenylbutene-2, 169
 2,3-Diphenylbutenes-2, 169-170, 376, 377
 1,4-Diphenylbutenyne, 177
 Diphenyl-di-*o*-benzylene-cyclobutanes, 199, 390, 391
 1,3-Diphenyl-1,3-di-(1-naphthyl)-propadiene, 174, 378
 1,1-Diphenylethylene, 164, 368
 1,2-Diphenylethylene (-Isostilbene and Stilbene), 164-167, 173, 368-375
 4,5-Diphenylglyoxaline, 164-165
 3,4-Diphenylhexanes, 159-160, 364, 365
 Diphenylindanes, 167, 168, 375, 377
 Diphenylindenes, 186, 384, 385
 1-Diphenylmethylene-3-benzylindene, 188, 387
 1-Diphenylmethylene-indane, 186, 384
 1,1-Diphenyl-3-methylindene, 174-175, 379
 2,4-Diphenyl-4-methylpentene-2, 172, 378
 1,3-Diphenyl-1- α -naphthyl-4:5-benzindene, 174, 379
 1,3-Diphenyl-3-(1-naphthyl)-3- α -naphthindene, 174, 379
 1,8-Diphenyloctatetraene-1,3,5,7, 179-180, 380, 381
 1,2-Diphenyl-(9-phenanthryl)-ethylene, 431
 (Diphenyl)phenethynylmethyl, 182-183
 1,2-Diphenyl-tetra-cyclohexylethane, 200, 390
 1,3-Diphenyl-1-*p*-tolyl-4:5-benzindene, 174, 379
 1,2-Diphenyl-3-*p*-tolylindene, 189, 386, 387
 2,3-Diphenyl-1-*p*-tolylindene, 189, 386, 387
 1,3-Diphenyl-3-*p*-tolyl-3- α -naphthindene, 174, 379
 1,3-Diphenyl-1-*p*-tolyl-3-(1-naphthyl)-propadiene, 174, 378
 1,3-Diphenyl-1-(1,1,3-triphenylpropargyl)-indene, 182-183, 383
 Diphenyltruxanes, 199, 390, 391
 1-(β,β -Diphenylvinyl)-2,3-di-*tert*-butyl-4-phenyl-naphthalene, 183-184, cf. 179, 383
 Dipinene, 118, 128, 129, 311, 323
 Dipropenyl (-Hexadiene-2,4), 73, 74, 275, 276, 277
p-Dipropenylbenzene, 164, 369
 Dipropylbenzenes, 158, 364, 365

Distillation, of isomers, 21
 Distyrene, 169, 376
 Diterpene, from camphene, 116, 311
 from *d*-limonene, 128-129, 323
 from *d*- α -pinene, 343
 from *l*- α -pinene, 144-145, 333, 349, 351
d-Diterpilene, 144, 345
l-Diterpilene, 345
 Dodecahydro-1,2-benzanthracene, 210, 397
 Dodecahydrophenanthrene, 148, 149, 352, 353
 Dodecahydrotriphenylene, 193, 194, 196, 389
 Dodecyne-1, 86, 286, 287
 Dodecyne-2, 86, 286, 287
 Durene, 156, 362

E

Echinocystic acid, 430
 Electromeric forms, 61
 Entropy of isomerization, 17, 427, 428
 Ethanol (See Alcohol)
 Ethylacetylene (-Butyne-1), 70, 82, 84, 269, 284, 285
 Ethylallene (-Pentadiene-1,2), 71, 268
 Ethylbenzene, 134, 154, 156, 327, 360
 Ethylbutene, 64, 260
 Ethyl chloride, 35, 236
 Ethylcyclohexane, 92, 94-95, 103, 302, 303
 1-Ethylcyclohexene-1, 109-110, 305
 Ethylcyclopentane, 98, 102, 103, 294, 295, 301
 Ethylcyclopropane, 52, 97, 292
 Ethylene, chlorination, 415-416
 Ethylidenecyclohexane, 109-110, 304
 1-Ethylidenecyclohexene-2, 128, 323
 Ethyl isofenchyl ether, 117, 311
 Ethyl isopropenyl ether, 70, 81, 269, 285
 Ethyl mercaptan, 166-167, 370, 372
 Ethylnaphthalenes, 191, 386, 387
 3-Ethylpentadiene-1,2, 73, 272
 3-Ethylpentadiene-1,3, 73, 273
 2-Ethylpentadiene-1,4, 75, 277
 3-Ethylpentane, 43-50, 427
 3-Ethylpentyne-1, 73, 273
 Ethylphenethylcarbinol, 162-163
sym-Ethyl-pseudocumene, 136, 329
 Ethyl terpinyl ether, 141, 341, 343
 1-Ethyltetralin, 163, 369
 1-Ethynylcyclohexene-1, 134, 326

F

Farnesenes, 78, 79, 280
 α -Fenchene, 117, 121, 310, 311, 317
 β -Fenchene, 116, 117, 120, 121, 310, 311, 317
 γ -Fenchene, 117, 120-121, 310, 311, 317
 δ -Fenchene, 121
 Fenchyl esters, 144-145, 347, 349
 Ferric (See Iron)
 Fire-bricks, 230
 Fischer and Koch's Co-Th catalyst, 141, 334
 Florida earth, 121, 316
 Floridin, action of on
 alkenyl benzenes, 172-173, 376
 alkynes, 89, 284, 286
 alkynyl benzenes, 181, 382
 allene, 70, 268
 allenic alkadienes, 73, 268-272
 butadiene-1,2, 70, 268
 n-butenes, 58, 248
 tert-butyl-allene, 72, 270
 butynes, 82, 84, 284, 286
 condensed aromatics, 386
 cyclenes, 134, 322
 dimethylhexadiene, 76, 278
 dimethylpentadienes, 72, 75, 270, 272, 276
 hexadiene-1,5, 73-74, 276
 limonene, 128, 322
 methylbutadiene, 71, 270
 methyltriphenylindane, 386
 phenylbutadiene, 175, 378
 4-phenylbutyne-1, 181, 382
 α -pinene, 334
 propadiene, 70, 268
 propyne, 82, 284
 tetraphenylbutene, 170, 376
 vinylcyclohexene, 128, 322

Flow diagram of isomerization plant, 433
 Fluorenes, 185, 189-190, 198, 201, 385-387, 393
 Fluorosulfonic acid, 32, 230
 9-Fluorylspirocyclopentane, 201, 393
 Formic acid, action of on
 alkapolyenes, 280
 camphorene, 132
 caryophyllene, 146, 352
 cedrene, 148, 352
 cycloisoprenemyrcene, 131, 324
 dimethylhexenylidene-indene, 185, 384
 farnesenes, 79, 280
 phyllocladene, 354
 α -pinene, 143, 144, 344
 rimuene, 149, 354
 sabinene, 115-116, 310
 sclarene, 147, 352
 sesquictronellene, 78-79
 squalene, 79, 280
 tetraphenylanthracene, 195, 388
 Free energy of isomerization, 17, 101
 Friedel-Crafts reactions, 33, 35, 190, 415, 431
 Fuller's earth, action of on
 carvomenthene, 320
 dipentene, 128-129, 322
 n-pentane, 230
 α -pinene, 140, 143, 334
 β -pinene, 118, 310

G

Gasoline,
 and isomerization, 19, 426, 432, 433
 determination of iso-alkanes in, 419
 from isobutane, 7, 426, 432-433, 442, 448, 450, 452, 453, 455
 isomerizations, 433, 441, 444-445, 449, 451, 453-454, 456, 458
 United States production, 7
 Geraniolene, 76, 278
 Glass (Durax, Pyrex, Suprax), isomerizations in of
 butenes, 244
 camphene, 116, 310
 Δ^3 -carene, 350
 cyclohexane, 99, 296
 cyclopropane, 95, 290
 hexadiene-1,5, 73, 274
 n-hexane, 30, 234
 isoöctenes, 262
 isostilbene and stilbene, 368, 374
 methylbutene, 256
 n-octane, 238
 octenes, 262
 4-phenylbutene-1, 161, 366
 α -pinene, 141-142, 330, 332, 334
 β -pinene, 117, 310
 Glukhov clay, 58, 248
 Glukhov kaolin, 334
 Gurjunene, 148, 149, 352
 Gustavson complexes, 32, 155, 230, 232, 442, 444, 446, 448, 455, 456, 459

H

Halosulfonic acid, 32, 230
 Heat of activation in isomerization, 56, 95, 167
 Heat of isomerization, 17, 31-33, 35, 58-59, 62, 95, 101, 114, 136-137, 166, 190, 426-427
 Heptadiene-1,2,
 from heptyne-1, 85, 287
 isomerizations, 72, 270
 Heptadiene-1,5, 74, 276
 Heptadiene-2,4, 74, 277
 Heptamethyleicosahydropicenes, 431
n-Heptane,
 antiknock value, 38
 from *n*-octane, 39, 241
 isomerizations, 28, 35, 36, 41, 236, 238
 (thermodynamic data), 43-50, 427
 Heptanes,
 isomerizations, 35, 41, 236, 238
 (thermodynamic data), 43-50, 427
 Heptenes, 66, 67, 262
 Heptyne-1,
 from heptadiene-1,2, 72, 271

Heptyne-1, from heptyne-2 and -3, 85, 287
 isomerizations, 85, 286
 Heptyne-2, 85, 286, 287
 Heptyne-3, 85, 286
 Heteropolar tautomer, 166, 173
 Hexaalkyl ethanes, 26
 Hexa-[*tert*-butylethynyl]-ethane, 86, 286, 288
 Hexadecane, 28
 Hexadecene, 69, 264, 266
 Hexadecyne-1, 86, 286, 287
 Hexadecyne-2, 86, 286, 287
 Hexadiene-1,2, 85, 287
 Hexadiene-1,3, 74, 277
 Hexadiene-1,4, 73, 74, 274-277
 Hexadiene-1,5, 73, 74, 274-277
 Hexadiene-2,4, 73, 74, 275, 276, 277
 Hexadiynes, 86, 286, 287
 4b,5,6,12c,13,14-Hexahydrobenzo[*c*]chrysene, 211, 397
 Hexahydrocadalene, 79, 281
 4b,5,6,10b,11,12-Hexahydrochrysene, 210, 397
 2,3,3a,10,11,11a-Hexahydro-1-cyclopenta[*a*]phenanthrenes, 201-202, 393
 3,4,4a,9,10,10a-Hexahydro-1,2,5,6-dibenzphenanthrene, 211, 397
 7a,8,9,10,11,11a-Hexahydro-11a-methyl-3,4-benzofluorene, 205, 395
 5,6,6a,13,14,14a-Hexahydropicene, 211, 397
 Hexa-(methyl-ethyl-pentynyl)-ethane, 87, 288
 2,6,10,15,19,23-Hexamethyltetracosahexaene-2,6,-10,14,18,22 (-Squalene), 79, 280
n-Hexane,
 analysis and determination, 407, 408-414, 416, 418
 antiknock value, 38
 from cyclohexane, 100, 101, 297
 dimethylbutane, 34, 237
 n-heptane, 35, 36, 237
 n-octane, 39-40, 241
 isomerizations, 28, 33, 40, 234
 (thermodynamic data), 35, 43-50
 Hexanes,
 isomerizations, 33, 40, 234, 236
 (thermodynamic data), 35, 43-50
 Hexaphenylethane, 159, 364
 1,3,3,4,4,6-Hexaphenylhexadiyne-1,5, 182-183, 382
 Hexenes, 63-64, 258-262
 Hexenylbenzene, 163, 368
 Hexyne-1, 85, 286, 287
 Hexyne-2, 85, 286, 287
 Hexyne-3, 74, 277
 Hydrindane, 113, 308
 Hydrindenepirocyclohexane, 203, 204, 393
 Hydriodic acid (See Hydrogen iodide)
 Hydrobromic acid (See Hydrogen bromide)
 Hydrocarbons (See also Alkanes, Alkenes, Alkynes, Aromatics, Cyclanes, Cyclenes, Cyclo-dienes, Gasoline, Isomerization, Petroleum)
 analysis of
 using antimony pentachloride, 407-419
 using parachor, 420
 isomerizations of (See Isomerization)
 number of isomers, 22, 23, 54, 81-83
 possibilities of isomerization, 400
 thermodynamics, free energy of isomerization, 17
 Hydrochloric acid (See Hydrogen chloride)
 Hydrogen, action of on
 alkanes, 29, 33, 34, 42, 219-241
 butenes, 244, 245
 hexene-1, 261
 l- β -pinene, 310
 Hydrogen atoms and heat of isomerization, 426
 Hydrogen bromide, action of on
 n-butane, 218
 cyclohexane, 292, 298
 cis-decalin, 308
 isostilbene, 166-167, 370, 372
 methylenecyclobutane, 108, 109, 304
 n-pentane, 31-32, 230
 tetraphenylpropadiene, 173, 378
 Hydrogen chloride, action of on
 alkanes, 28-40, 218-240
 cholestadienes, 150, 354
 cholestenes, 429, 430
 cryptomerene, 123

- Hydrogen chloride, action of on
 cyclohexanes, 292, 298-302
 dimethyl-methylene-cyclohexadiene, 135, 328
 dimethyl-phenethyl-cyclohexadiene, 213, 398
 dipentene, 129
 diphenylmethylene-indane, 186, 384
 gurjunene, 148, 352
 hexaphenylethane, 159, 364
 isostilbene, 166-167, 374
 mesitylene, 360
 methylene-methyl-dihydronaphthalene, 191, 386
 methylphenanthrylethyl-cyclohexene, 207
 methyl-phenyl-isopropenyl-cyclohexadiene, 213
 norhederabetulene, 430
 oleanene, 151, 354
 phenylbutadiene, 175, 380-381
 α -pinene, 143, 144, 334-340
 β -pinene, 119, 310, 312
 tetraphenylbutenes, 170-171, 376
 tetraphenyldibutyl-hexatetraene, 179, 380
 tetraphenylpropadiene, 173, 378
 α -thujene, 139, 330
 triphenylnaphthylpropadiene, 174, 378
 triphenylpropargyldiphenylindene, 182
 xylenes, 155, 356-360
 Hydrogen disproportionation, 44, 110, 129, 141, 148-149, 322-323, 330-333, 342-343
 Hydrogen iodide, action of on
 dihydrocamphene or isocamphane, 112-113
 methylenecyclohexane, 109, 304
 1-methylcyclohexene-1, 109, 318
 rubrene, 197, 390
 tetraphenylbutene, 171, 376
 Hydroquinone, 166-167, 370

I

- Identification and separation of isomers by distillation, 21
 Indanes, 185-189, 198, 203, 204, 209, 211-212, 384-387, 393, 395
 Indenes, 185-189, 198, 207-210, 384-387, 394, 396
 Industry, chemical, and isomerization of hydrocarbons, 7, 13
 Infusorial earth (See Kieselguhr)
 Inter-group isomerizations, 13, 55, 79, 118, 121, 122, 130, 132, 135, 142, 201-214
 Intramolecular rearrangement, 27
 Introduction, 13
 Introduction, general, 5
 Iodine, action of on
 β -carotene, 326
 cyclopropane, 96, 290
 dihydrocamphene or isocamphane, 112-113
 diphenylbutatriene, 177, 380
 diphenyldinaphthylpropadiene, 174, 378
 3,4-diphenylhexane, 159-160, 364
 diphenyloctatetrene, 180, 380
 1,2-diphenyl-1-(9-phenanthryl)-ethylene, 431
 isostilbene, 165-166, 370
 lycopene, 79-80, 282, 428
 l - α -pinene, 332
 polycopene, 428
 pseudo- α -carotene, 132-133, 324
 tetraphenylbutene, 170, 376
 tetraphenylpropadiene, 173, 378
 α -Ionane, 78, 281
 Iron,
 action of on
 cyclopropane, 96, 290
cis-decalin, 308
 isostilbene, 166-167, 370
 3-methylbutene-1, 256
 d - α -pinene, 140, 332
 bromination in presence of, 415
 Iron chloride, action of on
 dimethylbutylbenzenes, 158, 362, 364
 dimethylhexadiene, 76, 278
 m -xylene, 356
 Iron oxide, action of on
 methylbutene, 258
 pentene-2, 61, 254
 3-phenylpropene-1, 161, 366
 Iron phosphate, 266
 Iron sulfate, 143, 266

- Isoalkanes,
 determination of side-chains in alkanes by parachor, 420
 thermodynamic data, 32-33, 35, 43-50
 Isoamylalcohol and sodium (See Sodium isoamylate)
 Isoamylcyclohexane, 103, 105, 302
 Isobicyclocamphorene, 132, 325
 Isoborneol, 347
 Isobornyl chloride, 119, 120
 Isobornyl esters and ethers,
 from α -pinene, 144, 145, 337, 347, 349, 351
 from β -pinene, 118, 119, 120, 315
 Isobutane,
 alkylation by butenes, 442, 448, 450, 455
 antiknock value, 38
 from alkanes, 7, 29, 30, 31-35, 219-243, 427, 441-450, 452, 455-459
 from cyclohexanes, 100-101, 103, 301
 isomerizations, 28, 30, 31, 218-228, 434, 443 (equilibrium), 30, 43-50, 219-229
 thermodynamic data, 30-31, 43, 44-50
 key hydrocarbon for gasoline, 7
 Isobutene, 51-53, 58-59, 96, 247-253, 293, 441, 445-447, 450, 452
 Isobutylallene (-5-Methylhexadiene-1,2), 72, 270
 Isocadinene, 79, 147-148, 353
 Isocamphane, 112-113
 Isocamphanyl esters, 119, 143
 α -Isocaryophyllene alcohol, 146, 353
 β -Isocaryophyllene alcohol, 146, 353
 Isochrysofluorene, 192, 389
 Isodacrene, 150-151, 355
 Isodurene, 135-136, 156, 329, 360
 Isofenchyl acetate, 118, 313
 Isofenchyl alcohol, 317
 Isogurjunene, 148, 353
 Isoheptanes,
 from *n*-heptane, 35, 237, 239
 from *n*-octane, 37-40, 241
 thermodynamic data, 43-50
 Isohexane, 28, 34-36, 38, 41, 43, 101, 234, 235, 237, 261, 297, 299, 408, 409, 411-414, 416, 418
 Isohexanes,
 determination, 408-414, 418
 from cyclohexane, 100, 101, 297, 299
 from *n*-hexane, 33, 34, 235, 444, 449
 from *n*-octane, 37-40, 241
 thermodynamic data, 43-50
 Isolimonene, 128, 323
 Isomerization,
 allylic type of, 52-53, 72, 89, 110, 137, 161, 177-178, 186-188, 190, 191, 196, 214, 216, 366-367
 analysis of alkane isomers, 407, 416, 420
 and antiknock properties, 7
 and chemical industry, 7, 13
 by aromatization, 134-139, 239, 243, 297, 322-326, 327-329
 by chlorination followed by dechlorination, 451
 by cyclization, 63, 76-80, 108, 127, 129, 131-132, 145-147, 149-150, 160-163, 167-177, 179, 182-185, 190, 192-193, 195-199, 201-214, 256-257, 278-279, 280-281, 322-325, 328-329, 352-353, 366-369, 374-399
 by cyclization followed by decyclization, 25, 27, 34, 36-37, 52-53, 66, 88, 94-95, 100, 125
 by decyclization, 91, 93, 95-97, 108-109, 115-122, 125, 130, 139-145, 147-148, 153, 353
 by decyclization followed by cyclization, 93, 122, 125, 153, 189, 193-194, 196, 198
 by depolymerization followed by polymerization, 53-54, 124, 159, 200
 by polymerization, intermediary isomerization, and final depolymerization, 52
 by thermal treatment alone, 26-28, 68, 95, 142, 356-361
 definition, 13, 215
 methods, 21
 of, and catalysts for,
 alkanes, 24-50, 218-242, 427, 432-459 (thermodynamic data), 17, 31-33, 35, 43-50, 426-427
 alkenes, alkadienes, and alkapolyenes, 51-77, 244-283, 427-428, cf. 181-182
 alkenyl benzenes, 160, 172, 173, 366-378

Isomerization of, and catalysts for,
 alkynes, alkadiynes, and alkapolyynes, 81, 86,
 89, 90, cf. 181-182, 284-289
 alkynyl benzenes, 180-185, 382, 384
 anthracenes, 193-198, 388
 aromatic alkadienes, 173, 175, 177, 378, 380
 aromatic cyclanes, 199-200, 390
 aromatic cyclenes, 201, 392-396
 aromatic cyclodienes, 213, 398
 aromatic hydrocarbons, 152-185, 185-199, 199-
 214, 356-399, 431-432
 bicyclanes, 112-121, 308-315, 429
 bicyclenes, 139-146, 330-353, 429
 bicyclodienes, 147-148, 352
 condensed aromatics, 185-199, 384-390, 431-432
 cyclanes, 91-112, 290-307
 cyclenes, bicyclenes, and polycyclenes, 124,
 318-355, 429-431
 cyclodienes, 134, 135, 328
 fluorenes, 189-190, 198, 386
 hydrocarbons, 7, 21, 166, 167
 catalysts specified in several patents, 435-439
 (possibilities), 400
 (structural, geometrical, and optical), 13-14
 (thermodynamics), 17, 31-33, 35, 43-50, 426-
 428
 (unsolved problems), 26
 indanes and indenenes, 185-189, 198, 207-210,
 384, 386, 394, 396
 naphthacenes, 197, 199, 390
 naphthalenes, 190-193, 198, 378, 386, 388, 392,
 394
 pentacyclanes, 123
 pentacyclenes, 151, 354, 430-431
 phenanthrenes, 196, 198, 388, 390, 392, 394, 431
 spiranes, 112, 306-307, 428-429
 tetracyclenes, 150, 354, 429-430
 tricyclanes, 121-123, 316
 tricyclenes, 148, 352, 354
 Isooctane(s),
 as solvent, 368, 374
 determination, 408-414, 418
 from *n*-octane, 37, 39-42, 239, 241, 444
 Isopentane,
 antiknock value, 38
 as solvent, 368
 from *n*-butane, 27-28
 from *n*-octane, 39-40, 241
 from *n*-pentane, 31, 32, 229, 231, 233, 443-449,
 458-459
 isomerizations, 28, 32-33
 (equilibrium), 32, 43-50
 Isophyllocladene, 149-151, 355
 Isoprene (-2-Methylbutadiene-1,3), 71-73, 84,
 108-109, 269, 271, 287, 305, 440, 448
 Isoprenemyrcene, 131, 324, 325
 1-Isopropenyl-1,2,3,4-tetrahydronaphthalene, 192,
 386
 Isopropylacetylene (-3-Methylbutyne-1), 71-72,
 84, 271, 286
 Isopropylbenzene, 96
 1-Isopropylbenzylidene-3-benzylindene, 187-188,
 386, 387
 Isopropyl chloride, 35, 236
 Isopropylcyclohexane, 103-104, 302
 1-Isopropylcyclohexene-1, 110, 305
 Isopropylcyclopentane, 98, 294
 1-Isopropylcyclopentene-1, 109, 305
 Isopropylidenecyclohexane, 110, 304
 Isopropylidenecyclopentane, 109, 304
 1-Isopropylidene-1,2,3,4-tetrahydronaphthalene,
 192, 387
 7-Isopropyl-9-methyl-2,3-benzbicyclo[3.3.1]no-
 nene-2, 203, 393
 1-Isopropyl-4-methylcyclohexene-1, 126, 319
 1-Isopropyl-4-methyl-2,3-dihydrofluorene, 185,
 385
d-1-Isopropyl-4-methylene-bicyclo[3.1.0]hexane
 (-*d*-Sabinene), 115-116, 130, 310
d-1-Isopropyl-4-methylene-5-methylcyclopent-
 ene-1, 115-116, 311
 2-Isopropyl-4a-methyl-1,2,3,4,4a,11,12,12a-octa-
 hydrochrysene, 206, 395
 1-Isopropyl-2-(β -phenethyl)-4-methylcyclohex-
 ene-1, 204, 392

1-Isopropyl-2-phenylcyclopropane, 199, 390
 Isosciadopitene, 150-151, 355
 Isosquichamene, 149, 353
 Isostilbene, 164-167, 173, 368-375
 Isotriacyclocamphorene, 132, 325
 Isozingiberene, 131, 325

J

Japanese acid clay, 101, 143, 144, 296, 336
 Java citronella oil, 78-79

K

Kaolin (Glukhov kaolin), 143, 334
 Kaolinite, 29, 222
 Ketones, 139, 184, 322, 330, 382, 440
 Kieselguhr (Diatomaceous earth, Infusorial earth),
 action of on
 amylenes, 256
 n-butenes, 55-56, 59, 244, 248, 250
 1,1-diphenylethylene, 164, 368
 3-phenylpropene-1, 161, 366
 α -pinene, 143, 332, 334
 Kinetics, 15, 18, 19, 29, 30, 40, 58, 59, 64, 74, 95,
 165, 167, 218-225, 228-231, 240-247, 252-253,
 258-267, 274-279, 282-283, 296-297, 318-321,
 324-327, 356-359, 366-367

L

l-, 78
Ld, 144
 Latny clay, 336
 Lead oxides, 382
 Lead sulfate, 37, 240
 Light (Mazda lamp, Sunlight, Ultraviolet light),
 action of on
 diphenylbutadiene, 175, 380
 diphenylbutatriene, 177, 380
 diphenyloctatetrene, 179-180, 380
 isostilbene and stilbene, 165-167, 368, 370, 372,
 374
 pentene-2, 61, 252-257
 toluene, 356
 Lime (See Calcium oxide)
d- or *l*-Limonene,
 from *d*- or *l*- α -pinene, 141, 144, 333, 337, 343-
 351
 from *l*- β -pinene, 117-119
 isomerizations, 128-130, 138, 322
 racemization, 128, 322, 323
dl-Limonene,
 from limonene, 128, 323
 from β -pinene, 117, 118, 311, 315
 isomerizations, 128, 129, 130, 322, 323
 Linaloolene, 76, 77, 278
 Literature, of isomerization, 21, 427
 Lithium, action of on
 allylphenanthrene, 196, 388
 biphenylenephnylindene, 189, 386
 isostilbene, 165-166, 368
 tetraphenylbutene, 170, 376
 tetraphenylpropene, 168, 376
 triphenylnaphthalene, 193, 388
 triphenylpropene, 168, 376
 Lycopene, 79, 80, 280-283, 428

M

Magnesium acid phosphate, 312, 340
 Magnesium chloride, 76, 278
 Magnesium oxide, 132-134, 320, 324
 Magnesium phosphate, 320
 Magnesium sulfate, 126, 143, 266, 318, 336, 338
 Maleic anhydride, 135, 139-140, 328, 330, 429
 Manganese acid phosphate, 312, 338, 340
 Manganese oxide, action of on
 cyclohexene, 318
 2-methylbutene-2, 258
 pentene-2, 61, 254
 α -pinene, 332
 Manganese phosphate, 266
 Manganese sulfate, 266
 Mazda lamp, 252
dl-Menthene, 111, 126-127, 305, 320, 321

- Menthene-1, 126, 318, 320, 440
 Menthene-3, 126, 128-129, 321, 323, 440
 $\Delta^4(8)$ -Menthene, 111, 304
 Menthomenthene, 126, 319
 Mercury (See also Sodium amalgam), 151, 169, 354, 368, 376, 380
 Mercury chloride, 332
 Mercury oxide, 382
 Mercury sulfate, 342
 Mesitylene, 156, 360, 361, 363
 Metaboric acid, 143, 312, 338
 Metal halides, 414-415
 Metal oxides, 56, 244
 Metal salts, 126, 143, 266, 310, 312, 318, 320, 336, 338, 340, 435-439
 Metaphosphoric acid, 256
 Metavanadic acid, 312, 338
 Methane, 30, 40, 219, 221, 229, 243, 247, 253, 265, 285, 291, 295, 297, 309, 367, 415
 Methanolic potash (See Potassium methoxide)
 Methods, used in study of isomerization, 21
 (See also Isomerization)
 1-Methyl-2-(β -3'-acenaphthylethyl)cyclohexene-1, 206, 394
 Methylacetylene (-Propyne), 70, 81, 269, 284, 285
 Methylallene (-Butadiene-1,2), 70, 84, 268, 285
 Methylallylbenzenes, 163-164, 368
 1-Methyl-2-benzal-4-isopropenyl-cyclohexene-6, 213-214
 9-Methyl-2,3-benzbicyclo[3.3.1]nonene-2, 203, 393
 1-Methyl-2-benzylcyclohexene-1, 203, 392
 1-*p*-Methylbenzylidene-3-benzylindene, 187-188, 386, 387
 1-Methyl-2-benzyl-4-isopropenylcyclohexadiene-2,6, 213-214, 398
 1-Methyl-2-benzyl-4-isopropenyl-cyclohexadiene-3,6, 213-214
 1-Methyl-2-benzyl-4-isopropylbenzene, 213-214, 399
 1-Methyl-2-benzyl-4-isopropylcyclohexene-1, 203, 392
 1-Methylbicyclo[4.4.0]decane (-9-Methyldecalin), 114, 308, 309
 3-Methylbutadiene-1,2, 71-73, 84, 268, 270, 271, 287, 440
 2-Methylbutadiene-1,3 (-Isoprene), 71-73, 84, 108-109, 269, 271, 287, 305, 440
 2-Methylbutane, 31, 40, 43-50, 408-409, 433
 2-Methylbutene-1, 52, 61-63, 97, 256-259, 293
 3-Methylbutene-1, 52, 97, 256-259, 293
 2-Methylbutene-2, 52, 97, 256-259, 293, 439, 440
 Methylbutenes, 61-63, 256-259, 293, 439, 440
 1-Methyl-2-(3-butenyl)cyclohexene-1, 131, 324
 1-Methyl-2-(3-butenyl)cyclopentene-(1?), 127, 322
 2-Methyl-1-(3-butenyl)-3,4-dihydrophenanthrene, 196-197, 388, 390
 2-Methyl-1-butyl-phenanthrene, 196-197, 389, 391
 3-Methylbutyne-1, 71-72, 84, 271, 286, 287, 441
 Methylcyclobutane, 52, 97, 292
 1-Methylcyclobutene-1, 108-109, 305
 Methylcycloheptane, 106-107, 303
 Methylcyclohexane, determination, 418
 from cycloheptane, 106, 303
 from 1,2-dimethylcyclopentane, 99, 295
 from ethylcyclopentane, 98, 295
 from isoamylcyclohexane, 103, 303
 isomerizations, 101-104, 300, 301
 Methylcyclohexanols, 101-102
 Methylcyclohexanones, 101-102
 1-Methylcyclohexene-1, 109, 126, 305, 318
 4-Methylcyclohexene-1, 126, 318
 1-Methylcyclohexene-3, 126, 318
 Methylcyclohexenes, 101-102
 3-(β -[2-Methylcyclohex-1-en-1-yl]ethyl)acenaphthene, 206, 394
 1-(β -[2-Methylcyclohex-1-en-1-yl]ethyl)naphthalene, 205-206, 394
 1-(β -[2-Methylcyclohex-1-en-1-yl]isopropyl)naphthalene, 206, 394
 1-(2-Methylcyclohex-1-en-1-yl)-2-(α -naphthyl)propane, 206, 394
 Methylcyclopentane, from cyclohexane, 91, 93-94, 99-101, 103-104, 293-301, 428
 Methylcyclopentane, isomerizations, 97-98, 292-301
 1-Methyl-1,2-cyclopentano-1,2,3,4-tetrahydrophenanthrene, 202, 393
 Methylcyclopentene, 125-126, 319
 Methylcyclopentylcyclohexyl, 106
 Methylcyclopropane, 96, 292
 1-Methylcyclopropene-1, 125, 318
 9-Methyldecalin, 114, 308, 309
 4- and 6-Methyl-3',4'-dihydro-spiro-[indan-1,1'(2')-phenanthrenes], 211-212, 397
 1-Methyl-4-(1,5-dimethylhex-4-en-1-yl)cyclohexadiene-1,4, 138, 328
 1-Methyl-4-(1,5-dimethylhex-5-en-1-yl)cyclohexadiene-1,4, 138, 328
 1-Methyl-1,3-diphenylindene, 174-175, 379
 3-Methyl-1,1-diphenylindene, 174-175, 379
 4-Methyl-2,4-diphenylpentene-2, 172, 378
 4'-Methyldodecahydro-1,2-benzanthracene, 210, 397
 4-Methyl-5,6,6a,7,7a,8,9,10,11,11a,12,12a-dodecahydrobenz[a]anthrene, 210, 397
 Methylenecyclobutane, 108, 304
 Methylenecyclohexane, 109, 304
 1,3-Methylenecyclohexane, 109, 304
 Methylenecyclopropane, 108, 304
 Methylenedimethyl . . . (See Dimethylmethylenes . . .)
 (2 or 3)-Methylene-1-methylcyclopentanes, 126
 1-Methylene-2-methyl-1,4-dihydronaphthalene, 191, 386
 1-Methylene-2-methyl-3-isopropylcyclopentene-3, 115-116, 311
 3-Methylene-7-methyloctadiene-1,6 (-Myrcene), 78, 117-118, 280, 311
 Methylenetrimethyl . . . (See Trimethylmethylenes . . .)
 Methylethylacetylene (-Pentyne-2), 84, 284, 285
d-1-Methyl-2-ethyl-4-isopropenylcyclohexadiene-2,6, 138, 328
 1-Methyl-2-ethyl-4-isopropylbenzene, 138, 329
 3-Methyl-3-ethylpentane, 39
 3-Methylheptadiene-1,5, 75, 276
 3-Methylheptadiene-2,4, 75, 277
 5-Methylheptadiene-2,4, 75, 277
 2-Methylheptane, determination, 422-425, cf. 24
 from *n*-octane, 28, 41-42, 239
 isomerizations, 40, 242
 thermodynamic data, 427
 3-Methylheptane, 39
 thermodynamic data, 427
 4-Methylheptane, 408-414, 418
 Methylheptanes, 422-425, cf. 24
 6-Methylheptatriene-1,2,3, 77, 280
 6-Methylhepten-3-yne-1, 77, 281
 5-Methylhexadiene-1,2, 72, 270
 4-Methylhexadiene-1,3, 75, 277
 4-Methylhexadiene-1,4, 75, 277
 2-Methylhexadiene-1,5, 75, 276
 3-Methylhexadiene-1,5, 74, 75, 276, 277
 2-Methylhexadiene-2,4, 75, 277
 3-Methylhexadiene-2,4, 75, 277
 11a-Methyl-7a,8,9,10,11,11a-hexahydro-7-benzoc[*c*]fluorene, 205, 395
 Methylhexahydrochrysene, 196-197, 391
 3a-Methyl-2,3,3a,10,11,11a-hexahydro-1-cyclopenta[*a*]phenanthrene, 202, 393
 6b-Methyl-6b,7,8,9,10,10a-hexahydrofluoranthene, 205, 395
 2- and 4-Methyl-5,6,6a,13,14,14a-hexahdropicenes, 211-212, 397
 Methylhexane, 35, 237
 2-Methylhexane, antiknock value, 38
 from *n*-heptane, 36, 237
 thermodynamic data, 43-50, 427
 3-Methylhexane, from *n*-heptane, 36, 237
 thermodynamic data, 43-50, 427
 5-Methylhexyne-1, 72, 271
 Methylhydrindane, 113, 308
 2-(2-Methylindenyl-3)-1-(α -naphthyl)propane, 208, 394
 Methylisohexenylbenzofulvene, 185, 384
 Methylisopropenylbenzaldehyde, 213-214

- Methylisopropenylbenzylcyclohexadienes, 213-214, 398
- 1-Methyl-4-isopropenylcyclohexene-1 (See Limonene)
- 1-Methyl-4-isopropenylcyclohexene-2, 128-129, 323
- 1-Methyl-4-isopropenyl-2-phenylcyclohexadiene-2,6, 213, 398
- 9-Methyl-7-isopropyl-2,3-benzbicyclo[3.3.1]nonene-2, 203, 393
- Methylisopropylbenzylbenzene, 213-214, 399
- 1-Methyl-4-isopropyl-2-benzylcyclohexene-1, 203, 392
- d*-2-Methyl-5-isopropylbicyclo[3.1.0]hexene-2, (- α -Thujene), 139-140, 330
- 1-Methyl-4-isopropylcyclohexadiene-1,3 (- α -Terpinene), 134, 135, 139, 311, 313, 323, 328, 329, 331, 343, 345, 347, 349, 351
- 1-Methyl-4-isopropylcyclohexadiene-1,4 (- γ -Terpinene) 135, 139, 311, 313, 323, 328, 329, 331, 343, 345
- 1-Methyl-4-isopropylcyclohexadiene-1,5 (- α -Phellandrene), 130, 135, 139-140, 328, 331
- 1-Methyl-3-isopropylcyclohexene-1, 110, 305
- 1-Methyl-4-isopropylcyclohexene-1, 126, 318, 320
- d*-1-Methyl-4-isopropylcyclohexene-2, 126-127
- 1-Methyl-4-isopropylcyclohexene-3, 111, 126-127, 305, 320, 321
- 1-(β -[1-Methyl-4-isopropylcyclohex-1-en-2-yl]-ethyl)-naphthalene, 206, 394
- 4-Methyl-1-isopropyl-2,3-dihydrofluorene, 185, 385
- Methylisopropylidiphenyl, 213, 399
- Methylisopropylidiphenylmethane, 213-214, 399
- 1-Methyl-3-isopropylidenecyclohexane, 110, 304
- 1-Methyl-4-isopropylidenecyclohexane, 111, 304
- 1-Methyl-4-isopropylidenecyclohexene-1 (-Terpinolene), 128-130, 140-141, 144, 322-323, 333, 343, 345, 347, 349
- 4-Methyl-7-isopropyl-3-(β -1'-naphthylethyl)indene, 209, 394
- 4a-Methyl-2-isopropyl-1,2,3,4,4a,11,12,12a-octahydrochrysene, 206, 395
- 2-Methyl-4a-isopropyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene, 204, 393
- 4-Methyl-1-isopropyl-2-(β -phenethyl)cyclohexene-1, 204, 392
- 1-Methyl-4-isopropyl-2-phenylbenzene, 213, 399
- Methylmethylenes... (See Methylenemethyl...)
- Methylnaphthalenes, 191, 330, 386, 387
- 1-Methyl-2-(1'-naphthyl)cyclohexene-1, 205, 394
- 1-Methyl-2-(β -1'-naphthylethyl)cyclohexene-1, 205-206, 394
- 1-Methyl-2-(β -1'-naphthylethyl)cyclopentene-1, 202, 392
- 1-Methyl-1-(β -1'-naphthylethyl)cyclopentene-2, 202
- 2-Methyl-3-(β -1'-naphthylethyl)indene, 208, 394
- 1-Methyl-2-(β -1'-naphthylethyl)-4-isopropylcyclohexene-1, 206, 394
- 2-Methyl-1-(β -1'-naphthylisopropyl)-indanol-1, 208
- 2-Methyl-3-(β -1'-naphthylisopropyl)indene, 208, 394
- 1-Methyl-2-(2'-naphthylmethyl)cyclohexene-1, 205, 394
- 1-Methyl-2-(β -1'-naphthyl-*n*-propyl)cyclohexene-1, 206, 394
- 4a-Methyl-1,2,3,4,4a,11,12,12a-octahydrochrysene, 205-206, 395
- Methyloctahydrodibenzofluorenes, 432
- cis*-9-Methyl-1,4,5,6,7,8,9,10-octahydronaphthalene, 131, 325
- Methyloctahydronaphthofluorene, 209, 397
- 4a-Methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene, 204, 393
- 2-Methylpentane, action of antimony pentachloride, 408-414, 418
antiknock value, 38
determination, 418
formations and isomerizations, 33, 34, 36, 41, 234-237
thermodynamic data, 35, 43-50
- 3-Methylpentane, formations and isomerizations, 33, 34, 36, 41, 234-237
thermodynamic data, 35, 43-50
- Methylpentenes, 52, 64, 260, 261
- 1-Methyl-2-(β -9'-phenanthrylethyl)cyclohexene-1, 207, 394
- Methylphenbutylcarbinol, 163
- 1-Methyl-2-(β -phenethyl)cyclohexene-1, 204, 392
- 2-Methyl-3-(β -phenethyl)indene, 207-208, 394
- 2-Methyl-1-(β -phenethyl)-3- α -naphthindene, 211, 396
- Methylphenethyl-octahydronaphthalene, 210, 396
- 2-Methyl-1-(β -phenethyl)-6,7,8,9-tetrahydro-3-benz[e]indene, 431-432
- 2-Methyl-3-(β -phenethyl)-6,7,8,9-tetrahydro-1-benz[e]indene, 431-432
- Methylphenpropylcarbinol, 162-163
- Methylphenylbutenes, 162, 366, 367
- 1-Methyl-3-phenylindane, 169, 377
- 1-Methyl-2-phenyl-4-isopropenylcyclohexadiene-2,6, 213, 398
- 1-Methyl-2-phenyl-4-isopropylbenzene, 213, 399
- 2-Methylpropene-1 (-Isobutene), 51-53, 58-59, 96, 247-253, 293
- Methylpropenylbenzenes, 163-164, 369
- d*-1-Methyl-2-propyl-4-isopropenylcyclohexadiene-2,6, 138, 328
- 1-Methyl-2-propyl-4-isopropylbenzene, 138, 329
- Methyl salicylate, 144, 348
- 1-Methylsantene, 117, 121, 311, 316-317
- 2-Methylspiro[4.5]decene, 429
- 1-Methylspiro[4.4]nonane, 112, 307
- Methyltetrahydro-1,2,5,6-dibenzfluorene, 211, 397
- 3a-Methyl-3a,4,7,7a-tetrahydroindane, 127, 323
- 10-Methyl-3,4,10,11-tetrahydro-2',1'-naphtha-1,2-fluorene, 208, 395
- 11a-Methyl-5,6,6a,11a-tetrahydro-11-naphtho-[2,1-a]fluorene, 208, 395
- 2-Methyl-3-(β -[5,6,7,8-tetrahydro-1-naphthyl]-ethyl)indene, 209, 396
- 1-Methyltetralin, 162-163, 367, 369
- 1-Methyl-2,3,5-triphenylcyclopentanes, 199, 390, 391
- 1-Methyl-1,2,3-triphenylindane, 170, 377
- 1-Methyl-1,3,3-triphenylindane, 170, 188, 377, 386
- 1-Methyl-1,2,3-triphenylindene, 176, 381
- Molecular rearrangement, 27
- Molecular refraction, 21, 124
- Molybdates, 143, 312, 338
- Molybdenum disulfide, action of on
cyclohexane, 101, 296
cyclohexene, 126
n-heptane, 41, 238
n-hexane, 41, 234
methylcyclohexane, 102, 300
octahydroanthracenes, 193, 388
- Molybdenum, sulfur compound, 98, 101, 292, 296
- Molybdenum trioxide, 40, 101, 218, 296
- Molybdenum trisulfide, action of on
decalin, 114, 308
n-heptane, 41, 238
hexene-1, 63-64, 260
methylhydrindane, 113, 308
n-octane, 40, 42, 238
tetradecahydroanthracene, 122-123, 316
tetradecahydrophenanthrene, 122-123, 316
- Molybdic acids, 143, 312, 338, 340
- Monocycloparaffins, 91, 290
- Motor fuel, 7, 19, 37, 418, 420, 426, 433, 441-459
- Moving bed operation, 445
- Myrcene, 78, 117-118, 280, 311

N

- Naphthacenes, 197, 199, 390-391
- Naphthalene, 156, 357, 361, 367, 389
- Naphthalenes, 174, 179, 184, 190-193, 198, 201-202, 204-206, 208-210, 378-379, 386-389, 392, 394, 397
- 1-(1'-Naphthyl)cyclohexene-1, 204, 392
- 1-(β -1'-Naphthylethyl)cyclohexene-1, 205, 394
- 1-(β -1'-Naphthylethyl)cyclopentene-1, 201-202, 392
- 3-(β -1'-Naphthylethyl)-4-methyl-7-isopropylindene, 209, 394

1-(β -1'-Naphthylisopropyl)-2-methyl-indanol-1, 208
 1-(α -Naphthyl)-2-(2-methylindenyl-3)propane, 208, 394
 Neocarotene, 132-134, 324, 325, 326, 327
 Neo- α -carotene, 132-134, 324, 325, 326, 327
 Neolycopene, 79-80, 281-283, 428
 New tetrahedron, 57, 173
 Nickel, action of on
 butenes, 244, 246
 cycloheptane, 106, 302
 cyclooctane, 106, 302
 decalin, 308
 n-decane, 242
 dimethylbicyclooctenes, 129
 dimethylcyclohexanes, 105, 302
 isostilbene, 166-167, 370, 372
 octahydrophenanthrene, 196, 388
 n-octane, 238
 3-phenylpropene-1, 161, 366
 tetradecahydroanthracene, 122, 316
 tricyclene, 121-122, 316
 Nickel phosphate, 266
 Nickel sulfate, 143, 266, 310, 336, 338
 Nitric acid, action of on
 isostilbene, 167, 374
 Nitric acid, action of on
 phylloladene, 150-151, 354
 α -pinene, 338, 340
 β -pinene, 310, 312
 Nitrobenzene, 336, 441
p-Nitro-*m*-cresol, 144, 348
p-Nitrophenol, 144, 348
 Nonyne-1, 86, 287
 Nonyne-2, 86, 286
 Nopinene ($-\beta$ -Pinene), 117-120, 130, 143-144, 310-315, 441
 Norhederabetulenes, 430

O

Ocimene, 77, 280, 281
 Octadiene-2,6, 75, 276
 Octadiene-3,5, 75, 277
 Octahydroanthracenes, 193, 196, 388, 389
 1,2,3,4,4a,11,12,12a-Octahydrochrysenes, 205, 395
 1,2,3,4,5,6,6a,11a-Octahydro-7,11a-dimethyl-10-isopropyl-11-naphtho[2,1-a]fluorene, 210, 397
 1,2,2a,3,4,5,6,6a-Octahydro-6a-methylchrysene, 205-206, 395
 1,2,3,4,5,6,6a,11a-Octahydro-11a-methyl-11-naphtho[2,1-a]fluorene, 209, 397
 1,4,4a,5,6,7,8,8a-Octahydro-2-(*o*-methyl- β -phenethyl)naphthalene, 210, 396
 1,2,3,4,4a,5,8,8a-Octahydronaphthalene ($-\Delta^2$ -Octalin), 145-146, 350
 1,2,3,4,5,6,7,8-Octahydronaphthalene ($-\Delta^{9,10}$ -Octalin), 131, 145-146, 323, 351
 Octahydrophenanthrenes, 148, 193, 196, 203, 204, 353, 388, 389
 Δ^2 -Octalin, 145-146, 350
 $\Delta^{9,10}$ -Octalin, 131, 145-146, 323, 351
 Octamethyldotriacontatridecaene ($-\text{Lycopene}$), 79-80, 280-283, 428
n-Octane,
 analysis and determination, 408, 414, 416, 422-425
 antiknock value, 39
 isomerizations, 28, 37-42, 238, 240
 Octane number, and antiknock property of motor fuels, 7, 19, 37, 432-433
 Octane number of alkanes, 19, 38-39
 Octane rating, of gasoline, 7, 19, 37, 426, 432-433, 445, 450-451, 453-455
 Octanes,
 analysis and determination, 407, 418, 420, 423-425, cf. 21, 23, 24
 isomerizations, 37, 41, 238
 thermodynamic data, 427
 Octanthrene, 193, 196, 388, 389
 6-(4-[9-Octanthrenyl]butyl)-1,2,3,4-tetrahydronaphthalene, 193-194, 389
 1,1,2,3,4,5,6,6-Octaphenylhexadiene-1,5, 169, 377
 Octenes, 68-69, 262, 264, 441
 Octracene, 193, 196, 388, 389
 Octyne-1, 85-86, 286, 287

Octyne-2, 85-86, 286, 287
 Octyne-3, 86, 286
 Oil (See Petroleum)
 Oleanenes, 151, 354-355, 430-431
 Optical isomerization, 13-14, 23, 28, 52, 78-79, 126-128, 139, 148, 159-160, 174, 320-323, 330-331, 352-353, 364-365, 378-379
 Organic acids (See also Acids, and the specific acids, like Acetic acid), 118, 119, 144, 146, 312, 314, 338-350
 Orthoboric acid (See Boric acid)
 Orthophosphoric acid (See Phosphoric acid)
 Output, of airplane, and octane number, 20
 Oxalic acid, 128, 143, 312, 322, 338, 340, 346
 Oxonium compounds, 440
 Oxygen, 166-167, 368, 370

P

Palladium, action of on
 butenyl-methyl-dihydrophenanthrene, 196-197, 388
 dihydro-spiro-[indan-phenanthrene], 211-212
 3,7-dimethyloctene-1, 69, 264
 hexadiene-1,5, 73-74, 274
 isostilbene, 166-167, 372
 3-phenylpropene-1, 161, 366
 l- β -pinene, 118, 310
 Parachor, 420, cf. 21, 24, 33-34
 Patented processes, representative, 29, 58-59, 141, 143, 432-459
 Pentacyclanes, 123
 Pentacyclenes, 151, 354-355, 430, 431
 Pentadecane, 28
 Pentadiene-1,2, 71, 268
 Pentadiene-1,3, 74, 277
 Pentamethylbenzene, 137, 329
 Pentamethylcyclohexane, 103, 105, 303
n-Pentane,
 antiknock value, 38
 from *n*-butane, 27, 225
 from *n*-heptane, 35, 237
 from *n*-hexane, 33-34, 235
 from *n*-octane, 37, 39, 241
 isomerizations, 28, 31, 32, 33, 40, 228-235 (thermodynamic data), 43-50
 Pentanes,
 from *n*-heptane, 36, 237
 isomerizations, 31-32, 40, 228-234 (thermodynamic data), 32-33, 43-50
 1,1,3,3,3-Pentaphenylpropene, 169, 376
 Pentene-1, 52, 60-61, 252, 253, 255
 Pentene-2,
 from ethylcyclopropane, 97, 293
 from methylcyclobutane, 97, 293
 from methylenecyclobutane, 108-109, 305
 from pentyne-2, 84, 285
 isomerizations, 52, 61, 252
 Pentenes, 60-63, 252-259, 427-428, 439-440
 Pentenylbenzenes, 162-163, 366, 368, 369
 Pentyne-1, 71, 84, 269, 284, 285
 Pentyne-2, 84, 284, 285
 Perchloric acid, 55, 244
 Permutite (See also Sodium permutite, Zeolites),
 action of on
 n-butane, 29, 222, 224, 459
 n-butenes, 248, 441, 447
 3,3-dimethylbutene, 65, 260
 2-methylbutene-2, 63, 258
 n-octenes, 69, 264, 441
 pentenes, 60, 256, 258
 α -pinene, 143, 338
 β -pinene, 310
 Petroleum, 7, 19, 304, 306, 324, 326, 330, 354
 Petroleum ether, 79-80, 280
 α -Phellandrene, 130, 135, 139-140, 328, 331
 Phenanthrenes, 196, 198, 202-203, 206-207, 388-392, 394, 431
 1-(β -9'-Phenanthrylethyl)cyclohexene-1, 206, 394
 1-(β -9'-Phenanthrylethyl)cyclopentene-1, 202, 392
 9-Phenanthryl group repulsion, 431
 1-(β -Phenethyl)cyclohexene-1, 203, 204, 392
 1-(β -Phenethyl)-3,4-dihydro-naphthalene, 210, 396
 1-(β -Phenethyl)-3,4-dihydrophenanthrene, 211, 396

- 4-(β -Phenethyl)-1,2-dihydrophenanthrene, 211, 396
 3-(β -Phenethyl)indene, 207, 394
 1-(β -Phenethyl)-2-methyl-3- α -naphthindene, 211, 396
 1-(β -Phenethyl)-2-methyl-6,7,8,9-tetrahydro-3-benz[e]indene, 431-432
 3-(β -Phenethyl)-2-methyl-6,7,8,9-tetrahydro-1-benz[e]indene, 431-432
 1-(β -Phenethyl)naphthalene, 210, 397
 2-(β -Phenethyl)- Δ^2 -octalin, 210, 396
 Phenethynyl(diphenyl)methyl, 182-183
 Phenol, 143, 144, 348
 Phenols, substituted, 117, 143, 144, 166, 314, 348, 350, 370, 372, 374
 Phenylallene (-Phenylpropadiene), 173, 378
 Phenylbenzohydrylanthracene, 194, 195, 389
 10-Phenyl-9-benzohydryl-9,10-dihydroanthracene, 195
 10-Phenyl-9-benzohydrylidene-9,10-dihydroanthracene, 194, 195, 388
 Phenylbiphenylenebutenes, 189-190, 386, 387
 3-Phenyl-1-biphenylene-indene, 189, 386
 Phenyl- $[\beta,\beta$ -bis(β,β -diphenylvinyl)vinyl] methane, 177-178, 381
 Phenylene-bis-octracenybutane, 193-194, 389
 4-Phenylbutadiene-1,2, 181, 383
 1-Phenylbutadiene-1,3, 175, 378, 380, 381
 4-Phenylbutanol, 162
 Phenylbutenes, 161-162, 366, 367
 1-(4-Phenylbutyl)cyclopentene-1, 201, 392
 1-Phenylbutyne-1, 180-181, 383
 4-Phenylbutyne-1, 175, 180-181, 379, 382
 (*m*-[Phenylcyclohexylmethyl]-cyclohexyl)(phenyl)(di-cyclohexyl)methane, 200, 201, 391
 9-Phenyl-1,2,3,4-dibenzofluorene, 189, 387
 Phenyl-di-cyclohexylacetic acid, 200, 391
 Phenyldihydrodibenzanthracene, 193, 389
 9-Phenyl-9,10-dihydrophenanthrene, 167, 375
o-Phenyl-1,1-diphenylethylene, 167, 374
 Phenylene-bis-octracenybutane, 194
 6-Phenylhexene-1, 163, 368
 2-Phenylindene, 164-165, 185-186, 385
 3-Phenylindene, 185-186, 384
 Phenyl-lithium, 177-178, 380
 1-Phenyl-3-methylbutene-1, 162, 367
 1-Phenyl-3-methylbutene-2, 162, 366
 Phenyl-naphthalenes, 192, 386, 387, 388
 Phenylpentenes, 162-163, 366-369
 Phenylpropadiene, 173, 378
 Phenylpropenes, 161, 366, 367
 1-Phenylpropyne-1, 173, 180, 379, 382
 3-Phenylpropyne-1, 180, 383
 Phosgene, 441
 Phosphates, 56, 143, 244, 266, 312, 338, 340
 Phosphomolybdic acids, 143, 250, 312, 338, 340
 Phosphoric acid, action of on
 alkenes, 55-68, 244-266
 butenyl-methyl-dihydrophenanthrene, 196-197, 390
 butenylcyclohexanol, 131
 camphene, 116, 310
 cyclofenchene, 121, 316
 cyclohexenes, 125-131, 318-324
 dimethylphenethylcarbinol, 162
 limonene, 128, 322-323
 α -phellandrene, 135, 328
 1-phenyl-3-methylbutene-2, 162, 366
 α -pinene, 140, 143, 338-342
 β -pinene, 312
 α -terpinene, 134, 328
 Phosphorous acid, 312, 338
 Phosphorus, 143, 171, 332, 376
 Phosphorus pentachloride, 167, 374
 Phosphorus pentoxide, action of on
 butenylcyclohexanol, 131
 butenylcyclohexene, 131, 322
 butenyl-methyl-dihydrophenanthrene, 196-197, 390
 caryophyllene hydrate, 146-147
 dimethylbutenes, 65-66, 260, 262
 methylbutenylcyclopentene, 127, 322
 Δ^2 -octalin, 145-146, 350
 pinacolyl alcohol, 65-66
 Phosphostannic acid, 143, 312, 340
 Phosphotungstic acids, 143, 250, 312, 338, 340
 Phthalic acid, 143, 312, 338
 Phthalic anhydride, 121, 316
 Phthalyl chloride, 441
 Phyllocladene, 149-151, 354, 355
 Physics, 18
 Picric acid, 119, 143, 144, 314, 350
 α -Pinene, 117-119, 130, 140-144, 146, 311-315, 330-351, 429
 β -Pinene, 117-120, 130, 143-144, 310-315, 429
 Pinene hydrochloride, 119, 120
 Pipe clay (*See also* Clay), 29, 218, 222
 Piperidine, 189-190, 386
 Pirani gauge, 55
 Platinum, action of on
 p-allyltoluene, 163-164, 368
 cyclofenchene, 121, 316
 cycloheptane, 106
 cyclohexene, 126
 cyclooctane, 106-107, 302
 cyclopropane, 95-96, 290
 ethynylcyclohexene, 134, 326
 hexadiene-1,5, 74, 274
 isostilbene, 166-167, 372
 n-octane, 42, 238
 4-phenylbutene-1, 161, 366
 spirodecane, 112, 306
 tetramethyl-tetra-*tert*-butylethynyldecadiyne, 86-87, 288
 Platinum, hydrogenation by, 67, 87, 106, 126
 Polycyclanes, 91, 308-317
 Polymyrcenes, 281
 Porcelain clay (*See also* Clay), 218
 Porcelain tube, for isomerization of
 butene-1, 244
 cyclopropane, 95, 290
 ethylbenzene, 156, 360
 n-octane, 28, 238, 240
 β -pinene, 310
 xylenes, 356, 358
 Possibilities of hydrocarbon isomerization, 21-23, 54, 82-83, 400-405
 Potassium, 73, 77, 272, 280
 Potassium acid sulfate, 116, 117, 121, 310, 316
 Potassium chloride, 228
 Potassium dichromate, 354
 Potassium ferricyanide, 382
 Potassium hydroxide, 76, 278, 384, 386, 388
 Potassium hydroxide, alcoholic (Alcoholic potassium ash), 70; action of on
 allylnaphthalene, 191, 386
 allylphenanthrene, 196, 388
 butadiene-1,2, 70, 268
 butyne-1, 82, 284
 cyclohexylacetylene, 111, 304
 3,3-dimethylbutyne-1, 85, 286
 2,5-dimethylhexadiene-1,5, 75, 278
 1,2-diphenylindene, 186, 384
 diphenyltolylindene, 189, 386
 dodecyne-1, 86, 286
 heptyne-1, 85, 286
 hexadecyne-1, 86, 286
 hexadienes, 73, 74, 274, 276
 hexadiynes, 86, 286
 3-methylbutyne-1, 84, 286
 octyne-1, 85, 286
 pentyne-1, 84, 284
 1-phenylbutene-2, 162, 366
 1-phenyl-3-methylbutene-2, 162, 366
 1-phenylpentene-2, 163, 368
 phenylpropadiene, 173, 378
 3-phenylpropene-1, 161, 366
 propadiene, 70, 268
 propyne, 81, 284
 Potassium methoxide, 186-188, 384, 386
 Potassium permanganate, 134, 326
 Potassium persulfate, 382
 Power, of airplane and octane number, 20
 Preface, 7
 Prehnitene, 156, 360-363
 Prolycopene, 428
 Propadiene, 70, 81, 268, 269, 285
 Propane, 30, 40, 219, 221, 225, 227, 229, 233, 237, 247, 253, 265, 267, 303, 457, 458
 Propene, 36, 52, 55, 91, 93, 95-96, 244, 285, 291
 Propenylallyl- (*See* Allylpropenyl-)

Propenylbenzene, 161, 366, 367
 Propenylcyclohexane, 107, 110, 305
 Propenylmethyl- (*See* Methylpropenyl-)
 1-Propenyl-naphthalene, 191, 387
 9-Propenylphenanthrene, 196, 389
 Propenyltoluenes, 163-164, 369
 Propylacetylene (-Pentyne-1), 71, 84, 269, 284, 285
n-Propylbenzene, 96, 366
 Propyl bromide, 33, 234
 Propyl chloride, 33, 35, 234, 236, 240, 415
n-Propylcyclohexane, 103-104, 302
 1-Propylcyclohexene-1, 107, 110, 305
 Propylcyclopentane, 98, 294, 295
 1-*n*-Propyl-2,4-dimethylbenzene, 157, 362
 1-*n*-Propyl-3,4-dimethylbenzene, 136, 329
 Propylidenecyclohexane, 107, 110, 304
 Propyne, 70, 81, 269, 284, 285
 Pseudo- α -carotene, 132-134, 324-327
 Pseudocumene, 135, 156, 286, 329, 357-363
 Pseudoionane, 78, 280
 Pseudorubrene, 197, 199, 391
 Pumice, action of on
 benzyl-naphthalene, 192, 388
 n-butane and isobutane, 29, 218-222
 butene-1, 244
 butyne-1, 84, 284
 carvomenthene, 126, 318, 320
 condensed aromatics, 185, 384
 2,3-diphenylbutene-2, 376
 heptyne-1, 85, 286
 hexene-1, 65, 260
 3-methylbutene-1, 62, 256
 octenes, 68, 264
 phenylindene, 185, 384
 α -pinene, 330, 334, 340, 342
 tolylindene, 185, 384
 Pyrex (*See* Glass)
 α -Pyronene, 141-142, 331, 333
 β -Pyronene, 141-142, 331, 333
 Pyrophosphoric acid, 248, 256
 Pyrophyllite, 218
 Pyrosulfuric acid, 122, 316

Q

Quartz, 155, 218, 244, 262, 294, 304, 356, 358
 Quillaic acid, 151
 Quinoline, 109, 126, 270, 304, 318
 Quinoline hydriodide, 109, 126, 304, 318
 Quinoline hydrobromide, 71-72, 270
 Quinone, 139-140, 330

R

Raman spectra, 21, 428
 Rearrangements (*See* Wagner rearrangements)
 References, 461
 Refraction, 21, 124, 149, 420
 Resorcinol, 144, 348
 Retropinacol rearrangement, 121
 Reversibility of isomerization, 15, 55, 98, 106, 122, 133-135, 156, 158-159, 161, 164-167, 170, 180, 187-189, 193, 195-196, 216, 366-375, 400-405, 431
 Rimuene, 149-150, 354, 355
 Rubber, 426, 440-441
 Rubrene, 197, 199, 390

S

Sabinene, 115-116, 130, 310
 Salicylic acid, 118-119, 143, 314, 348
 Salts, 117, 126, 143, 310, 312, 318, 336, 338, 340
 Sciadopitene, 149-151, 354, 355
 Sclarene, 147, 352
 Sclareol, 147
 Sea-foam stone (*See also* Silicates), 218
 Selenium, 208, 432
 Selinenes, 147, 352, 353
 Semibenzenes, 135, 328
 Separation, of isomers, 21
 Sequence of isomerization, 16, 34, 37, 52-53, 61, 66, 72-73, 76, 79, 86, 100, 107, 130, 132-133, 136-137, 139, 140, 156, 171, 181-182, 184
 Sesquichamene, 149, 352
 Sesquictronellene, 78

Sesquiterpenes, 78-79, 124, 131, 138, 146-149, 280
 Side-chains, determination, 420-425
 Side reactions, 16, 29, 32-36, 39-40, 54, 68-69, 100, 155-157, 167, 180, 216
 Silex, 332
 Silica (*See also* Alumina), action of on
 butenes, 56, 59, 244, 246
 cyclohexene, 125-126, 318
 hexadecene, 69, 264, 266
 n-hexane, 234
 limonene, 129, 322
 octenes, 68, 69, 264
 n-pentane, 230
 pentenes, 60, 61, 252
 phylloladene, 354
 α -pinene, 143, 334
 Silica gel, action of on
 alkyl-naphthalenes, 191, 386
 n-butane and isobutane, 29, 222
 n-butenes, 248
 carvomenthene, 126, 318
 cyclohexene, 125-126, 318
 dimethylbutenes, 65-66, 260, 262
 4-methylcyclohexene-1, 126, 318
 1-methyl-4-isopropyl-cyclohexene-3, 127, 320
 phenyl-naphthalene, 192, 386
 3-phenylpropene-1, 161, 366
 pinacolyl alcohol, 65-66
 α -pinene, 338
 β -pinene, 310
 Silicates (*See also* Alumina, Silica), 56, 244, 248, 252
 Silicic acids (*See also* Alumina, Silica, Silica gel), 143, 312, 338, 340
 Silicious earth, 256
 Silicotungstic acids, 143, 312, 340
 Silicovanadic acids, 143, 312, 340
 Silver-lined steel apparatus, 42, 238
 Slurry-type operations, 445
 Sodamide (*See* Sodium amide)
 Sodium, action of on
 butadiene-1,2, 70, 268
 dimethylpentadienes, 72, 73, 270, 272
 dodecyne-2, 86, 286
 3-ethylpentadiene-1,2, 73, 272
 hexadecyne-2, 86, 286
 hexaphenylethane, 159, 364
 hexyne-2, 85, 286
 isostilbene, 165-166, 368
 3-methylbutadiene-1,2, 71, 270
 methylenecyclobutane, 108, 304
 octyne-2, 85-86, 286
 pentyne-2, 84, 284
 propadiene, 70, 268
 tetraphenylbutadiene, 176, 380
 tetraphenylbutenes, 171, 172, 376, 378
 tetraphenylpropene, 169, 376
 triphenylindene, 188, 386
 vinylidenecyclohexane, 110, 304
 Sodium acid sulfate, 121-122, 143, 312, 316, 338
 Sodium amalgam, action of on
 biphenylenephenylindene, 189, 386
 diphenyltetracyclohexylethane, 200, 390
 diphenyltolylindenes, 189, 386
 tetramethyltetraphenyldecadiyne, 181-182, 183, 184, 185, 384
 tetraphenyldibutylhexatetraene, 179, 380
 Sodium amide, 89; action of on
 cyclohexylalkynes-2, 304, 306
 heptadiene-1,2, 72, 270
 heptyne-2, 85, 286
 heptyne-3, 85, 286
 5-methylhexadiene-1,2, 72, 270
 nonyne-2, 86, 286
 octyne-2, 85-86, 286
 octyne-3, 86, 286
 pentadiene-1,2, 71, 268
 1-phenylpropyne-1, 180, 382
 Sodium ethoxide, action of on
 biphenylene-phenyl-butene, 189-190, 386
 dihydronaphthalene, 190, 386
 isopropenyl-tetrahydronaphthalene, 191-192, 386
 methylcyclohexanone semicarbazones, 102
 tetraphenylbutyne, 181, 382
 tetratolylbutyne, 181, 382

- Sodium followed by alcohol (for demetalation),
 action of on
 benzohydrylidene-phenyl-dihydroanthracene,
 194, 388
 benzohydryl-phenyl-anthracene, 195
 isostilbene, 165, 166, 368
 tetraphenylbutenes, 171-172, 376, 378
 Sodium hydroxide (Soda-lime), 85, 89, 286
 Sodium hydroxide, alcoholic (Alcoholic soda, *See*
also Sodium ethoxide), action of on
 alkynes, 81
 dihydronaphthalene, 190, 386
 isopropenyltetrahydronaphthalene, 191-192, 386
 tetraphenylbutyne, 181, 382
 tetratolylbutyne, 181, 382
 Sodium isoamylate, 138, 197, 328, 376, 390
 Sodium permutite (*See also* Permutite, Zeolites),
 action of on
n-butane and isobutane, 29, 222, 224
n-butenes, 248
 dimethylbutenes, 65-66, 260
 octenes, 69, 264
n-pentenes, 60, 256
 Sodium tungstate, 310, 312, 338
 Spectra, 21, 428
 Speed, of airplane, and octane number, 20
 Spiranes, 91, 112, 306
 Spirocyclane, 108
 Spiro[4.5]decane, 112, 306, 307
 Spirodecenes, 428-429
 Spiropentane, 108
 Squalene, 79, 280
 Stannic... (*See* Tin...)
 Steam (*See also* Water), 248, 250, 252, 264, 310,
 312, 332, 338, 340, 360, 362, 364
 Stearin, 119, 314
 Steel, vessel for isomerization, 30, 234, 238, 308
 Stilbene, 164-167, 173, 368-375
 Stilbene-dilithium, 165-166, 368
 Stilbene-disodium, 165-166, 368
 Strained versus "strainless" molecules, 18, 55, 95-
 96, 101-102, 106-107, 112, 115-116, 118, 145,
 203, 428
 Structural isomerization, 13-14, 16, 55, 101, 134-
 135, 153, 201-213, 215-216
 Styrene, 156, 361
 Styrylbis(β,β -diphenylvinyl)methane, 177-178, 380
 Sulfates, 266
 Sulfide catalysts, 40-42, 63-64, 98, 101-102, 113-
 114, 122-123, 126, 193, 234, 238, 260, 292, 296,
 300, 308, 316, 388, 443-444, 459
 Sulfonic acids, 127, 143, 174, 244, 312, 320, 338, 346,
 378
 Sulfur, 41-42, 296
 Sulfuric acid,
 action of on
 alkylidenecyclohexanes, 109, 304
 alkylphenethylcyclohexene, 204, 392
 alkyl-tetrahydronaphthylethyl-indenes, 209,
 210, 396
 benzylisopropenylmethylcyclohexadiene, 213,
 398
 biphenylene-diphenyl-butadiene, 190, 386
 cadinene, 147-148, 352
 α -camphorene, 132, 324
 caryophyllene, 146-147, 352
l- β -curcumene, 138, 328
 cyclofenchene, 316
 cyclopropane, 96
 dihydromyrcene, 76, 77, 278
 dihydroterpinolene, 304
 2,2-dimethylbutane, 236
 dimethylnonatriene, 78, 280
 dimethyloctatriene, 77-78, 280
 2,4-dimethylpentane, 41, 238
 dimethylrubrene, 197, 390
 dipentene, 129, 322
 diphenylbutenes, 169, 170, 376
 ethylphenethylcarbinol, 162-163
 farnesenes, 79, 280
 fenchenes, 116, 310
 geraniolene, 76, 77, 278
 gurjunene, 148, 352
 isopropenylmethylphenethylcyclohexadiene, 213,
 398
 isopropylidenecyclopentane, 109, 304
 Sulfuric acid,
 action of on
 isopropylmethylphenethylcyclohexene, 204, 392
 isopropylphenethylcyclopropane, 199, 200, 390
 linaloolene, 76, 77, 278
 3-methylbutene-1, 62-63, 256
 methylenecyclobutane, 108-109, 304
 methylpentanes, 41, 234, 236
 methylphenpropylcarbinol, 162-163
 methyl-tetrahydronaphthylethyl-indene, 209,
 396
 pentaphenylpropene, 169, 376
 α -phellandrene, 135, 328
 phenethylindene, 394
 phenylbutylcyclopentene, 201, 392
 6-phenylhexene-1, 163, 368
 1-phenyl-3-methylbutene-2, 162, 366
 phenylpentenes, 162-163, 366, 368
 phyllocladene, 150-151, 354
 α -pinene, 140, 141, 143, 342, 344
 β -pinene, 118, 312
 pseudoionane, 78, 280
 sabinene, 115, 310
d- α -selinene, 147, 352
 sesquichamene, 149, 352
 squalene, 79, 280
 tetraethylbenzenes, 158, 364
 tetramethylbenzenes, 156, 360, 362
 1,1,2,6-tetramethyl-4-methylenecyclohexa-
 diene-2,5, 137, 328
 tetraphenylbutadiene, 176, 380
 1,1,3,3-tetraphenylbutene, 170, 376
 tetraphenyldibutylhexatetraene, 380
 tricyclodecane, 122, 316
 trimethylethylbenzenes, 157, 362
 1,1,3-trimethyl-4-ethylidene-cyclohexadiene-
 2,5, 136, 328
 1,1,2-trimethyl-4-methylene-cyclohexadiene-
 2,5, 135-136, 328
 triphenylbutadiene, 174, 378
 1,1,3-triphenylpropene-1, 167-168, 374
 zingiberene, 131, 324
 for alkylation (by alkenes), of
 alkanes, 26-27
 benzene, 60, 63
 Sulfur trioxide, 362
 Summary of known isomerizations, 215-216, 400-
 405
 Sunlight, 61, 165, 166, 175, 177, 179-180, 254-255,
 368-372, 380
 Suprax (*See* Glass)
 Surface tension, 420, 421-425
 Sylvestrene, 145, 351
- ### T
- Tables of isomerization (*See* Isomerization), 218-
 400
 Terpenes, 77, 78, 115-116, 117, 121, 129, 280, 281,
 311, 337, 339, 449-451
 Terpinene,
 from dipentene and *d*-limonene, 128-129, 323
 from α -phellandrene and sabinene, 115-116, 130,
 311, 329
 from α -pinene, 140, 141, 144, 333, 335, 341, 343,
 345
 from β -pinene, 118, 313
 from terpinolene, 130, 323
 α -Terpinene,
 from *d*- Δ^4 -carene, 145, 351
 from dipentene, 128-129, 323
 from *d*-limonene, 128-129, 138, 323
 from α -phellandrene and sabinene, 115-116, 130,
 311, 329
 from *d*- and *l*- α -pinenes, 140-145, 333, 343, 345,
 347, 349
 from γ -terpinene, 135, 329
 from terpinolene, 130, 136-138, 323
 from α -thujene, 139, 331
 unisomerized by phosphoric acid, 135, 328
 γ -Terpinene, 135, 328, 329
 from dipentene, 129, 323
 from *d*-limonene, 128-129, 323
 from α -phellandrene and sabinene, 115-116, 130,
 311, 329
 from terpinolene, 130, 322
 from α -thujene, 139, 331

- Terpinene dihydrochloride, 115-116, 331
 Terpinene monohydrochloride, 139, 331
 Terpeneol, from α -pinene, 141, 335, 341, 343, 345
 Terpeneol-4, salts from *d*-sabinene, 115-116, 311
 Terpin hydrate, 144, 341, 343, 345, 347
 Terpinolene,
 from dipentene, 128-130, 323
 from *d*-limonene, 128-129, 138, 323
 from *d*- and *l*- α -pinenes, 140, 141, 144-145, 333, 343, 345, 347
 isomerizations, 130, 136-138, 322
 Terpinyl esters, 144-145, 337, 345, 347, 349
 Tetrachloroethane, 346
 Tetracyclane, 91
 Tetracyclenes, 150, 354, 429-430
 Tetracyclosqualene, 79, 281
 Tetradecahydroanthracene, 122, 123, 316, 317
 Tetradecahydrophenanthrene, 122, 123, 148, 316, 317
 Tetradecane, 28
 Tetraethylbenzenes, 158, 364, 365, 431
 Tetrahydrocaryophyllene, 429
 5,6,6a,11a-Tetrahydrochrysofluorene, 207, 395
 Tetrahydrocyclopentenotriphenylene, 202, 393
 Tetrahydro-di-cyclopentadiene, 121, 122, 316
 1,2,3,4-Tetrahydro-5-(β -2,4-dimethyl-7-isopropyl-3-indenyl)ethyl)naphthalene, 210, 396
 5,6,6a,11a-Tetrahydro-11a-methylchrysofluorene, 207-208, 395
 5,6,6a,13a-Tetrahydro-13a-methyldibenzo[ag]-fluorene, 211, 397
 1,2,3,4-Tetrahydro-5-(β -[2-methyl-3-indenyl]-ethyl)naphthalene, 209, 396
 Tetrahydronaphthalene, 162, 163
 Tetralin, 162, 163
 Tetralyl-octanthrenyl-butane, 193-194, 389
 Tetramethylallene (-2,4-Dimethylpentadiene-2,3), 72, 73, 75, 137, 270, 271
 Tetramethylanthracene, 359
 Tetramethylbenzenes, 135-136, 156, 329, 357-363, 431
 2,2,3,3-Tetramethylbutane,
 antiknock value, 39
 isomerization, 28
 1,2,6,6-Tetramethylcyclohexadiene-1,3 (- β -Pyrene), 141-142, 331, 333
 Tetramethylcyclohexanes, 98, 103, 105, 295, 303
 2,2,9,9-Tetramethyl-5,6-di-*tert*-butyl-5,6-diphenyldecadiene-3,7, 183
 Tetramethyldi-*tert*-butylethynyl-di-*tert*-butyl-tetradecatetraene-diyne, 86-87, 287, 289
 Tetramethylmethane,
 antiknock value, 38
 from *n*-pentane and isopentane, 32-33
 isomerizations, 28, 32-33, 234
 1,1,2,5-Tetramethyl-4-methylenecyclohexadiene-2,5, 137, 328
 1,1,2,6-Tetramethyl-4-methylenecyclohexadiene-2,5, 137, 139, 328
 2,2,9,9-Tetramethyl-5,5,6,6-tetra-biphenyldecadiene-3,7, 184, 384
 Tetramethyltetra-*tert*-butylethynyldecadiene, 86-87, 286, 288
 2,2,9,9-Tetramethyl-5,5,6,6-tetraphenyldecadiene-3,7, 181-185, 382
 Tetraphenylallene, 173, 378
 1,4,9,10-Tetraphenylanthracene, 195, 388
 1,1',3,3'-Tetraphenyl-1,1'-biindene, 182-183, 383
 1,1,2,3-Tetraphenylbutadiene-1,3, 176, 380
 1,1,4,4-Tetraphenylbutadiene-1,3, 181, 383
 1,2,3,4-Tetraphenylbutadiene-1,3, 176, 380
 1,2,3,4-Tetraphenylbutane, 176, 381
 Tetraphenylbutene, 170-172, 376, 377
 1,1,4,4-Tetraphenylbutyne-2, 181, 382
 1,1,3,3-Tetraphenylcyclobutane, 170, 188, 377, 386
 1,1,6,6-Tetraphenyl-3,4-di-*tert*-butyl-hexatetraene-1,2,4,5, 179, 183-184, 380, 383
 2,6b,8,12b-Tetraphenyl-6b,12b-dihydrochrysene, 183, 383
 1,1,3,3-Tetraphenylindane, 169, 377
 5,6,11,12-Tetraphenylnaphthacene (-Rubrene), 197, 199, 390
 1,1,5,5-Tetraphenyl-3-phenethylidene-pentadiene-1,4, 177-178, 381
 Tetraphenylpropadiene, 173, 378
 Tetraphenylpropenes, 168-169, 376, 377
 1,1,5,5-Tetraphenyl-3-styrylpentadiene-1,4, 177-178, 380
 1,1,4,4-Tetra-*p*-tolylbutadiene-1,3, 181, 383
 1,1,4,4-Tetra-*p*-tolylbutyne-2, 181, 382
 Thermal isomerization, 26-28, 55, 58, 60, 68, 95, 142, 151, 155-156, 240, 244, 252, 290, 354, 356-361
 Thermodynamics
 and isomerization, 16-18, 21, 30-33, 35, 43-50, 58-59, 62, 95, 101, 114, 136-137, 166-167, 190, 426-428
 Thiophenol, 166-167, 374
 Thorium, 334
 Thorium dioxide, 60-67, 140, 143, 252, 260, 262, 264, 318, 334
 α -Thujene, 139-140, 330
 Tikhvin bauxite, 143, 332
 Tin (See also Phosphostannic acid)
 Tin chloride, 170, 171, 172, 176, 207, 213, 214, 376, 378, 380, 394, 398, 440, 443, 449, 456
 Titanic acids, 143, 312, 338, 340
 Titanium dioxide, 56, 126, 244, 294, 318
 Toluene,
 as solvent, 314, 350, 384
 from benzene, 154
 from cycloheptane, 106
 from ethylbenzene, 156, 361
 from xylenes, 155-156, 357, 359
 ultraviolet absorption spectrum, 154
p-Toluenesulfonic acid, 127, 174, 320, 378
 Tollyl-diphenyl... (See Diphenyl tolyl...)
 Tollylethylidihydrophenanthrenes, 212, 396
 2-(β -*o*-Tollylethyl)- Δ^2 -octalin, 210, 396
 2-*p*-Tollylindene, 185-186, 385
 3-*p*-Tollylindene, 185-186, 384
 Tonsil, 126, 320
 Tribromophenol, 144, 350
 Trichlorophenol, 118-119, 144, 314, 350
 Tricyclanes, 121-123, 316
 Tricyclene, 121, 122, 316
 Tricyclenes, 121, 148, 149, 352-354
 Tricyclocamphorene, 132, 325
 Tricyclo[5.2.1.0^{2,6}]decane, 121, 122, 316
 Tricyclogurjunene, 148, 352
 Tricyclosqualene, 79, 281
 Tricyclotetradecanes, 122-123, 316, 317
 Tridecane, 28
 Triethylbenzenes, 431
 Trimethylbenzenes, 135, 156, 329, 357-363
 2,2,3-Trimethylbicyclo[2.2.1]heptane, 112-113
 1,2,3-Trimethylbicyclo[2.2.1]heptene-2 (1-Methylsantene), 116, 117, 121, 311, 317
 2,5,5-Trimethylbicyclo[2.2.1]heptene-2 (- γ -Fenchene), 117, 121, 311, 317
 3,7,7-Trimethylbicyclo[4.1.0]heptene-2 (- Δ^4 -Carene), 145, 350
 3,7,7-Trimethylbicyclo[4.1.0]heptene-3 (- Δ^3 -Carene), 145, 350
 2,2,3-Trimethylbutane,
 antiknock value, 39
 from *n*-heptane, 36, 237
 thermodynamic data, 43-50, 427
 1,5,5-Trimethyl-6-(1-butenyl)cyclohexene-1 (- α -Ionane), 78, 281
 1,2,4-Trimethylcyclohexane, 98, 295
 1,3,5-Trimethylcyclohexane,
 action of aluminum chloride, 103-104, 302
 from *n*-, *sec*-, and *tert*-butyl cyclopentanes, 98, 295
 from *n*-propyl and isopropylcyclohexanes, 103-104, 303
 (Trimethylcyclohexenyl)-tetramethyl-(trimethylcyclohexenyl)-octadecanonaene (-Pseudo- α -carotene), 132-134, 324-327
 Trimethylcyclopropane, 99-100
 3,7,11-Trimethyldodecatetraene-1,3,6,10 (- α -Farnesene), 78-79, 280
 1,2,4-Trimethyl-3-ethylbenzene, 157, 363
 1,2,4-Trimethyl-5-ethylbenzene, 157, 362
 1,2,5-Trimethyl-4-ethylbenzene, 136, 329
 1,3,5-Trimethyl-2-ethylbenzene, 157, 362
 Trimethylethylene (-2-Methylbutene-2), 52, 61-63, 97, 256, 258, 293
 1,1,3-Trimethyl-4-ethylidenecyclohexadiene-2,5, 136, 328
 1,1,2-Trimethylindane, 199, 391

1,1,2-Trimethyl-4-methylenecyclohexadiene-2,5, 135-136, 328
 1,5,5-Trimethyl-6-methylenecyclohexene-1, 78, 142
 1,2,3-Trimethylnorcamphene-2 (-1-Methylsantene), 116, 117, 121, 311, 317
 2,5,5-Trimethylnorcamphene-2 (- γ -Fenchene), 117, 121, 311, 317
 2,7,7-Trimethylnorcamphene-2, 121
 5,7,7-Trimethylnorcamphene-2, 121
 2,2,3-Trimethylpentane, antiknock value, 39
 2,2,4-Trimethylpentane, analysis and determination, 424, cf. 24
 antiknock value, 37, 39
 chlorination, 23
 isomerizations, 40, 242
 thermodynamics, 426-427
 2,3,4-Trimethylpentane, antiknock value, 39
 from *n*-octane, 41-42
 2,3,4-Trimethylpentene, 69, 265
 2,4,4-Trimethylpentenes, 51, 264, 265
 1,1,3-Trimethyl-3-phenylindane, 172, 379
 1,3,3-Trimethyl-tricyclo[2.2.1.0^{2,6}]heptane (-Cyclofenchene), 121, 316
 2,3,3-Trimethyl-tricyclo[2.2.1.0^{2,6}]heptane (-Tricyclene), 121, 122, 316
 2,4,5-Trinitro-*m*-cresol, 144, 350
 Trinitrothymol, 144, 350
 1,1,3-Triphenyl-4:5-benzindene, 174, 379
 1,1,2-Triphenyl-2-benzylethylene, 169, 377
 1,1,3-Triphenylbutadiene-1,2, 174-175, 378
 1,1,3-Triphenylbutadiene-1,3, 174-175, 379
 1,2,4-Triphenylcyclopentanes, 199, 390, 391
 1,2,3-Triphenylindane, 168, 377
 Triphenylindenes, 173, 188, 379, 386, 387
 Triphenylmethane, 159, 365
 Triphenylmethyl, 159, 364
 1,2,3-Triphenylnaphthalene, 193, 388
 1,3,3-Triphenyl-3- α -naphthindene, 174, 379
 Triphenyl-(1-naphthyl)-propadiene, 174, 378
 4,9,10-Triphenyl-1,9-(*o*-phenylene)-9,10-dihydroanthracene, 195, 389
 5,11,12-Triphenyl-5,6-(*o*-phenylene)-5,12-dihydronaphthacene (-Pseudorubrene), 197, 199, 391
 1-(1,1,3-Triphenylpropargyl)-1,3-diphenylindene, 182-183, 383
 Triphenylpropenes, 167-168, 374-377
 Tripropylbenzenes, 158, 364, 365, 442
 Tungstic acids, 143, 312, 338, 340
 Turpentine oil, American and French (See α -Pinene)
 Russian (See α - and β -Pinenes)
 Types of isomerization, 13-15, 400-405

U

Ultraviolet absorption spectrum, 56, 154, 164, 179
 Ultraviolet light, 14, 61, 165, 254, 256, 354, 356, 368, 374
 Uranium acid phosphate, 312, 340

V

Vanadic acids, 143, 312, 318, 338, 340
 Vaseline, 71, 72, 268, 270
 β -Vetivane, 115, 308
 1-Vinylcyclohexene-1, 110, 305
 1-Vinylcyclohexene-3, 128, 322
 Vinylcyclopropane, 108

Vinylidenecyclohexane (-Cyclohexylideneethyl-ene), 110, 111, 304, 305

W

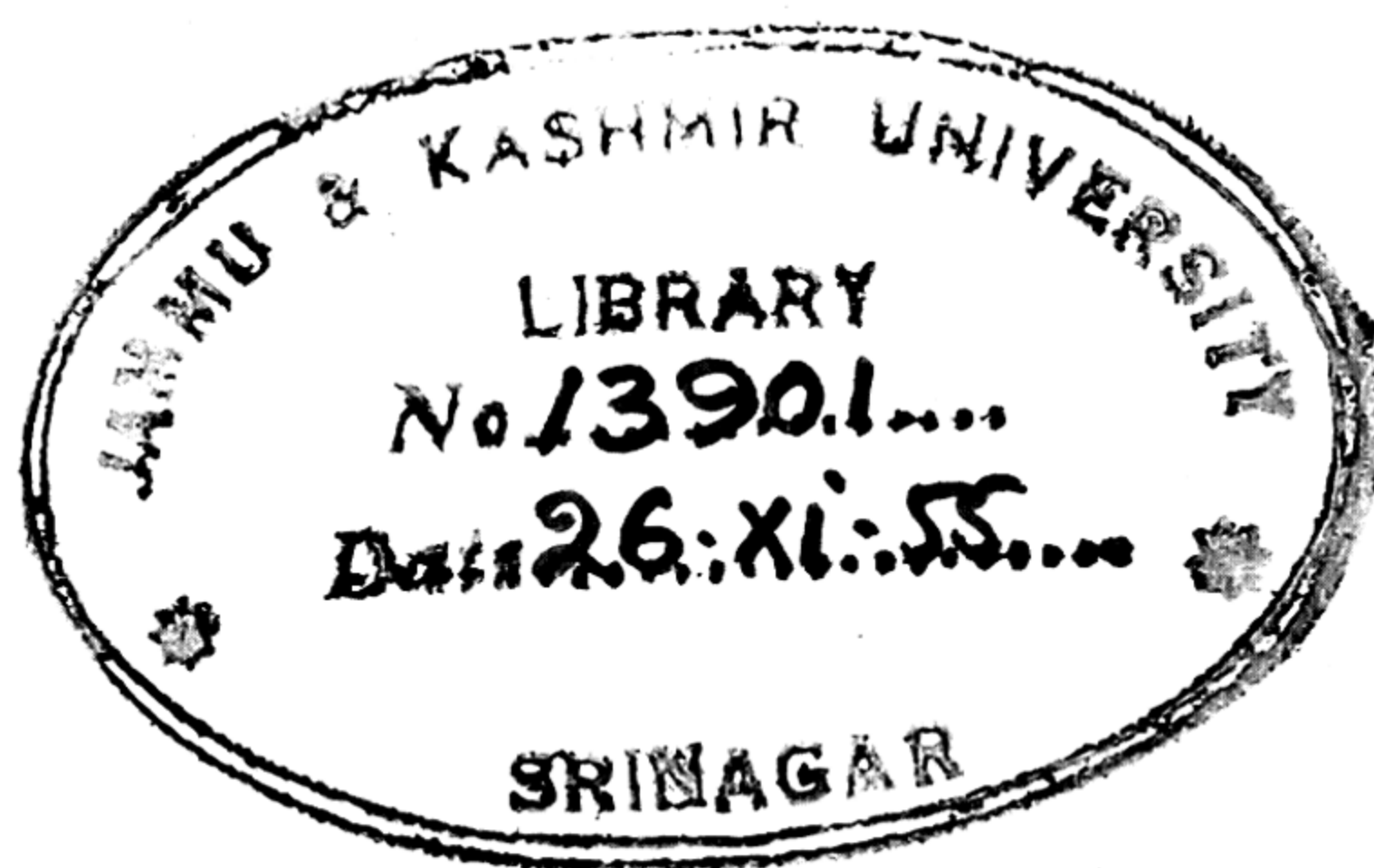
Wagner rearrangements, 117, 119, 143-144, 311, 315
 Walden inversion, 57
 War, and Octane number, 19
 Water (See also Steam, Sulfuric acid, and the other individual acids), action of on *d*-limonene, 322
 Water with Acids
 (with Acetic acid), action of on *l*- α -pinene, 346
 (with Benzene sulfonic acid), action of on butene-1, 244
 (with Formic acid), action of on α -camphorene, 324
 cycloisoprenemyrcene, 324
 phyllocladene, 354
l- α -pinene, 344
d-rimuene, 354
 (with Hydrogen chloride), action of on isostilbene, 374
 (with Perchloric acid), action of on butene-1, 244
 (with Phosphoric acid), action of on 1-phenyl-3-methylbutene-2, 366
 (with Sulfuric acid, See Sulfuric acid)
 Water with Aluminum chloride, action of on alkanes, 29, 31, 228-238
 cyclohexane, 97-98, 100, 292, 298, 428
 with zinc chloride, action of on butene-1, 244

X

Xylene, as solvent, 61, 72, 159, 183, 252, 254, 268, 270, 288, 314, 336, 382, 390
m-Xylene, as solvent, 159, 364
 from 1,3-dimethyl-4-butylated benzenes, 158, 363
 from *o*- and *p*-xylenes, 152, 155-156, 356-361
 isomerizations, 356-359
o-Xylene, 152, 155-156, 356-357, 359, 361
p-Xylene, 152, 155-156, 361
 Xylenes, 152, 155-156, 356-361

Z

Zeolites (See also Permutite, Sodium permutite), 29, 126, 222, 224, 252, 320, 439
 Zinc, 151, 354, 430
 Zinc bromide, 108-109, 304
 Zinc chloride, action of on butene-1, 55, 244
 cyclopropane, 290
 cyclohexane, 294
n-heptane, 42, 238
 hexene-1, 65, 260
n-octane, 40-42, 240
 octenes, 68, 262, 264
l- α -pinene, 346
 Zinc hydroxybromide, 108-109, 304
 Zinc oxide, 42, 238
 Zinc sulfate, 143, 266, 336
 Zingiberene, 131, 324
 Zirconium dioxide, 318
 Zirconium tetrachloride, 40, 232



American Chemical Society
MONOGRAPH SERIES

PUBLISHED

No.

1. **The Chemistry of Enzyme Action (Revised Edition).** By K. George Falk.
2. **The Chemical Effects of Alpha Particles and Electrons (Revised Edition).**
By Samuel C. Lind.
3. **Organic Compounds of Mercury.** By Frank C. Whitmore. (Out of Print)
4. **Industrial Hydrogen.** By Hugh S. Taylor. (Out of Print)
5. **Zirconium and Its Compounds.** By Francis P. Venable.
6. **The Vitamins (Revised Edition).** By H. C. Sherman and S. L. Smith.
7. **The Properties of Electrically Conducting Systems.** By Charles A. Kraus.
8. **The Origin of Spectra.** By Paul D. Foote and F. L. Mohler. (Out of Print)
9. **Carotinoids and Related Pigments.** By Leroy S. Palmer.
10. **The Analysis of Rubber.** By John B. Tuttle. (Out of Print)
11. **Glue and Gelatin.** By Jerome Alexander. (Out of Print)
12. **The Chemistry of Leather Manufacture (Revised Edition).** By John A. Wilson.
Vol. I and Vol II.
13. **Wood Distillation.** By L. F. Hawley. (Out of Print)
14. **Valence and the Structure of Atoms and Molecules.** By Gilbert N. Lewis.
(Out of Print)
15. **Organic Arsenical Compounds.** By George W. Raiziss and Jos. L. Gavron.
16. **Colloid Chemistry (Revised Edition).** By The Svedberg.
17. **Solubility (Revised Edition).** By Joel H. Hildebrand.
18. **Coal Carbonization.** By Horace C. Porter. (Revision in preparation)
19. **The Structure of Crystals (Second Edition) and Supplement to Second Edition.** By Ralph W. G. Wyckoff.
20. **The Recovery of Gasoline from Natural Gas.** By George A. Burrell. (Out of Print)
21. **The Chemical Aspects of Immunity (Revised Edition).** By H. Gideon Wells.
22. **Molybdenum, Cerium and Related Alloy Steels.** By H. W. Gillett and E. L. Mack.
23. **The Animal as a Converter of Matter and Energy.** By H. P. Armsby and C. Robert Moulton.
24. **Organic Derivatives of Antimony.** By Walter G. Christiansen.
25. **Shale Oil.** By Ralph H. McKee.
26. **The Chemistry of Wheat Flour.** By C. H. Bailey.
27. **Surface Equilibria of Biological and Organic Colloids.** By P. Lecomte du Noüy.
28. **The Chemistry of Wood.** By L. F. Hawley and Louis E. Wise. (Out of print)
29. **Photosynthesis.** By H. A. Spoehr. (Out of Print)

American Chemical Society Monograph Series

PUBLISHED

No.

30. **Casein and Its Industrial Applications (Revised Edition).** By Edwin Sutermeister and F. L. Browne.
31. **Equilibria in Saturated Salt Solutions.** By Walter C. Blasdale.
32. **Statistical Mechanics as Applied to Physics and Chemistry.** By Richard C. Tolman. (Out of Print)
33. **Titanium.** By William M. Thornton, Jr.
34. **Phosphoric Acid, Phosphates and Phosphatic Fertilizers.** By W. H. Waggaman.
35. **Noxious Gases.** By Yandell Henderson and H. W. Haggard. (Revision in preparation)
36. **Hydrochloric Acid and Sodium Sulfate.** By N. A. Laury.
37. **The Properties of Silica.** By Robert B. Sosman.
38. **The Chemistry of Water and Sewage Treatment.** By Arthur M. Buswell. (Revision in preparation)
39. **The Mechanism of Homogeneous Organic Reactions.** By Francis O. Rice.
40. **Protective Metallic Coatings.** By Henry S. Rawdon. Replaced by **Protective Coatings for Metals.**
41. **Fundamentals of Dairy Science (Revised Edition).** By Associates of Rogers.
42. **The Modern Calorimeter.** By Walter P. White.
43. **Photochemical Processes.** By George Kistiakowsky.
44. **Glycerol and the Glycols.** By James W. Lawrie.
45. **Molecular Rearrangements.** By C. W. Porter.
46. **Soluble Silicates in Industry.** By James G. Vail.
47. **Thyroxine.** By E. C. Kendall.
48. **The Biochemistry of the Amino Acids.** By H. H. Mitchell and T. S. Hamilton. (Revision in preparation)
49. **The Industrial Development of Searles Lake Brines.** By John E. Teeple.
50. **The Pyrolysis of Carbon Compounds.** By Charles D. Hurd.
51. **Tin.** By Charles L. Mantell.
52. **Diatomaceous Earth.** By Robert Calvert.
53. **Bearing Metals and Bearings.** By William M. Corse.
54. **Development of Physiological Chemistry in the United States.** By Russell H. Chittenden.
55. **Dielectric Constants and Molecular Structure.** By Charles P. Smyth. (Out of Print)
56. **Nucleic Acids.** By P. A. Levene and L. W. Bass.
57. **The Kinetics of Homogeneous Gas Reactions.** By Louis S. Kassel.
58. **Vegetable Fats and Oils.** By George S. Jamieson. (Out of print) (Revised edition in preparation)
59. **Fixed Nitrogen.** By Harry A. Curtis.

American Chemical Society Monograph Series

PUBLISHED

No.

60. **The Free Energies of Some Organic Compounds.** By G. S. Parks and H. M. Huffman. (Out of Print)
61. **The Catalytic Oxidation of Organic Compounds in the Vapor Phase.** By L. F. Marek and Dorothy A. Hahn.
62. **Physiological Effects of Radiant Energy.** By H. Laurens.
63. **Chemical Refining of Petroleum.** By Kalichevsky and B. A. Stagner. (Second Edition.)
64. **Therapeutic Agents of the Quinoline Group.** By W. F. Von Oettingen.
65. **Manufacture of Soda.** By T. P. Hou. (Revised Edition)
66. **Electrokinetic Phenomena and Their Application to Biology and Medicine.** By H. A. Abramson.
67. **Arsenical and Argentiferous Copper.** By J. L. Gregg.
68. **Nitrogen System of Compounds.** By E. C. Franklin.
69. **Sulfuric Acid Manufacture.** By Andrew M. Fairlie.
70. **The Chemistry of Natural Products Related to Phenanthrene (Second Edition with Appendix).** By L. F. Fieser.
71. **The Corrosion Resistance of Metals and Alloys.** By Robert J. McKay and Robert Worthington.
72. **Carbon Dioxide.** By Elton L. Quinn and Charles L. Jones.
73. **The Reactions of Pure Hydrocarbons.** By Gustav Egloff.
74. **Chemistry and Technology of Rubber.** By C. C. Davis and J. T. Blake.
75. **Polymerization.** By R. E. Burk, A. J. Weith, H. E. Thompson and I. Williams.
76. **Modern Methods of Refining Lubricating Oils.** By V. A. Kalichevsky.
77. **Properties of Glass.** By George W. Morey.
78. **Physical Constants of Hydrocarbons.** By Gustav Egloff. Vols. I and II.
79. **Protective Coatings for Metals.** By R. M. Burns and A. E. Schuh.
80. **Raman Effect and its Chemical Applications.** By James H. Hibben.
81. **Properties of Water.** By Dr. N. E. Dorsey.
82. **Mineral Metabolism.** By A. T. Shohl.
83. **Phenomena at the Temperature of Liquid Helium.** By E. F. Burton. H. Grayson Smith and J. O. Wilhelm.
84. **The Ring Index.** By A. M. Patterson and L. T. Capell.
85. **Photodynamic Action and Diseases Caused by Light.** By Harold Francis Blum.
86. **Photochemistry of Gases.** By W. A. Noyes, Jr., and P. A. Leighton.
87. **Anhydrous Aluminum Chloride in Organic Chemistry.** By Charles A. Thomas.

American Chemical Society Monograph Series

IN PREPARATION

- Piezo-Chemistry. By L. H. Adams.
- The Chemistry of Coordinate Compounds. By J. C. Bailar.
- Constituents of Wheat Flour. By Clyde H. Bailey.
- Water Softening. By A. S. Behrman.
- The Biochemistry of the Fats and Related Substances. By W. R. Bloor.
- Ions, Dipole Ions and Uncharged Molecules. By Edwin J. Cohn.
- Proteins in Metabolism and Nutrition. By George E. Cowgill.
- The Refining of Motor Fuels. By G. Egloff.
- Organometallic Compounds. By Henry Gilman.
- Animal and Vegetable Waxes. By L. W. Greene.
- Surface Energy and Colloidal Systems. By W. D. Harkins and T. F. Young.
- Raw Materials of Lacquer Manufacture. By J. S. Long.
- Chemistry of Natural Coloring Matters. By F. Mayer.
- Acetylene. By associates of the late J. A. Nieuwland.
- Furfural and other Furan Compounds. By F. N. Peters, Jr., and H. J. Brownlee.
- The Chemistry of Aliphatic Orthoesters. By Howard W. Post.
- Aliphatic Sulfur Compounds. By E. Emmet Reid.
- Electrical Precipitation of Suspended Particles from Gases. By W. A. Schmidt and Evald Anderson.
- Dipole Moments. By C. P. Smyth.
- Potash in North America. By J. W. Turrentine.
- Formaldehyde. By J. Frederic Walker.
- Precise Electric Thermometry. By W. P. White and E. F. Mueller.
- Colloidal Carbon. By W. B. Wiegand.
- The Chemistry of Leather Manufacture (Supplement). By J. A. Wilson.
- Measurement of Particle Size and Its Application. By L. T. Work.
- Physical Chemistry of Electrolytic Solutions. By H. E. Harned and B. Owen.
- Wood Chemistry. By L. F. Hawley and Louis A. Wise.

**THE JAMMU & KASHMIR UNIVERSITY
LIBRARY.**

DATE LOANED

Class No. 541.92 **Book No.** 58 I

Vol. _____ **Copy** _____

Accession No 13901

--	--	--	--

